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July 1976

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POTENTIAL ENVIRONMENTAL CONSEQUENCES OF TERTIARY OIL RECOVERY

FINAL REPORT

JULY, 1976

U.S. ENVIRONMENTAL PROTECTION AGENCY
OFFICE OF PLANNING AND EVALUATION
WASHINGTON, D.C. 20460

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Certain environmental risks are associated with the implementation of tertiary oil recovery; one goal in the development of this technology should be to minimize its environmental cost. A cost/benefit analysis of the environmental impacts and economic gains is not possible until the potential risks have been identified. This report delineates the types of environmental problems which may occur.

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Potential environmental problems associated with the so-called tertiary or enhanced oil recovery methods (micellar-polymer flooding, polymer flooding, surfactant flooding, hydrocarbon miscible displacement, carbon dioxide miscible displacement, steam displacement (or drive), cyclic steam stimulation, and in-situ combustion (or fireflooding)) are identified. Possible impacts on ambient air quality, groundwater supplies and water quality are assessed qualitatively, and where possible quantitatively, using dispersion modeling and risk estimates. The report examines those potential problems which are unique to enhanced oil recovery as well as post-operational problems such as chemical degradation products. Forecasts of enhanced oil recovery activity are allocated by process and region for use in impact analysis. Research needs are described to evaluate the problem areas.

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ib.

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CHAPTER ONE

INTRODUCTION AND SUMMARY

1.0 Introduction

Tertiary oil recovery processes may contribute 20 to 60 billion barrels of additional reserves to the Nation's domestic supplies in known oil fields within the next 25 years.[1] The resource potential of tertiary or enhanced recovery is likely to play an important supplementary role in fulfilling the country's needs for petroleum.

Because the techniques will usually be applied in previously delineated and well-developed oil fields, the economic risks of recovering tertiary oil are different from the risks faced in off-shore and continental shelf oil and gas exploration. Tertiary oil recovery processes will be applied in the field on the basis of favorable expected economic returns for a given project.

Certain environmental risks are associated with the implementation of tertiary oil recovery; one goal in the development of this technology should be to minimize its environmental cost. A cost/benefit analysis of the environmental impacts and economic gains is not possible until the potential risks have been identified. This report delineates the types of environmental problems which may occur.

1.1 Conclusions

As identified in Chapter Two, the processes for tertiary oil recovery may pose the types of problems to the environment shown on Table 1-1. In addition, the application of each process may result in secondary impacts such as off-site manufacture of chemicals, transportation of bulk chemicals, and refinery load shifts to handle the higher average sulfur content in lower gravity crudes.

In comparison with exploratory and developmental drilling and conventional oil production, tertiary oil recovery

---

[1] Production forecasts for enhanced oil recovery which are summarized here are discussed in detail in Chapter Three.

TABLE 1-1

TERTIARY OIL RECOVERY

POTENTIAL ENVIRONMENTAL PROBLEM AREAS

PROCESS	PROBLEM	CAUSES
Steam Displacement	Air Quality	SO_x and particulates from steam generators. Hydrocarbons from producing wells and other field sources
	Water Quality	Spills, leaks of chemical foaming agents (if used)
	Water Supplies	Process water demand
In-Situ Combustion	Air Quality	Hydrocarbons and CO from producing wells
	Water Quality	Spills, leaks of low pH water with heavy metals
Micellar-Polymer Flooding	Water Quality	Spills, reservoir and well leaks, disposal of chemically-loaded brines
	Air Quality	On-site manufacturing of chemicals
	Solid Wastes	On-site manufacturing of chemicals
	Water Supplies	Process water demand
Carbon Dioxide	Air Quality	Fugutive emissions of H_2S combined with CO_2.
	Water Quality	Low pH water with H_2S Spills, leaks

projects pose different environmental problems. Much more is known about the subsurface geology by the time an enhanced recovery project is started. Delineation of the reservoir has resulted from in-fill drilling following the original discovery and additional detailed geologic data are compiled and analyzed before the project. The high pressures which may cause "blow-outs" in exploratory wells have been reduced during earlier petroleum production operations so that this risk is essentially eliminated in tertiary recovery. In terms of potential magnitude of environmental problems, the tertiary recovery processes examined in this study can be roughly ranked as follows in descending order of environmental concern: steam displacement, in-situ combustion, micellar-polymer flooding, miscible carbon dioxide.

The thermal methods of enhanced oil recovery may pose air quality problems if large-scale development occurs in an oil field. A high density development oil field steam generator burning 1 percent sulfur fuel can exceed National Ambient Air Quality Standards for sulfur dioxide. Such impacts may represent a stumbling block to the full realization of the resource potential by thermal oil recovery methods. Unanswered questions remain regarding emissions of hydrocarbons from steam displacement and in-situ combustion. Potential sources of these emissions may include wellheads and produced water treatment systems as well as fugitive and area sources. Further data are required to characterize the emissions from these sources in order to identify control technology needs. In some cases the recovery of casing blow gases containing oil condensate can be accomplished profitably, thus improving the economic return of the project while protecting the environment from these emissions.

Micellar-polymer floods involve large quantities of expensive chemicals some of which could have an adverse affect on the environment if improperly handled. Economic factors should tend to mitigate environmental risks during the operations phase of a micellar-polymer flood. Well failures or improper injection profiles which could result in the loss of expensive chemicals or poor reservoir response must be prevented if the project is to be profitable. Engineering studies are carried out in the early phases of a project to identify and appraise these problems. Since the front-end investment in such projects is large and the returns in many cases are marginal, every effort would be made to minimize foreseeable fluid losses and thus risks to the subsurface environment. Disposal of chemically-laden produced water should also be carried out in an environmentally acceptable manner. Field data on the concentrations of chemicals in the produced fluid streams is needed to determine the need for effluent control systems.

1.1.1 Water Supplies and Water Quality Conclusions

Operational chemical flooding projects such as micellar-polymer flooding pose few hazards to underground water supplies because numerous physical and chemical processes as shown in Figure 1-1 mitigate chemical leaks or spills. At present, petroleum sulfonate surfactants are the commonly-used materials which could have the most adverse impact on water supplies and water quality. However, these materials are susceptible to adsorption and precipitation within the oil reservoir as much or more than any other chemical used. Subsurface leaks from miscible carbon dioxide projects using CO_2 containing some H_2S could contaminate groundwater supplies. Although no known problems of this type have occurred to date as a result of enhanced oil recovery operations, hydrogen sulfide contamination of groundwater supplies has occurred as a result of conventional petroleum production operations.[1]

Future hazards from completed chemical flood projects should be of the same small magnitude as the risks from ongoing recovery projects despite the fact that additional mechanisms associated with well age tend to increase the chances of leaks.

The two most significant potential causes of water quality deterioration during tertiary oil recovery are: (1) spills of chemicals as a result of transportation and handling, and (2) improper disposal of chemically-loaded produced water. Both sources are difficult to control by further regulation. Considerable volumes of fresh water from existing or potential water supplies may be required to carry out large-scale projects for steam displacement and to a greater extent for chemical methods of oil recovery such as micellar-polymer flooding. Although this does not appear to be a barrier to early development activities, impacts on water supplies may occur due to local shortages or encroachment of salt water into some aquifers.

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[1] Personal communication with Mr. Love, City Secretary, Lulling, Texas.

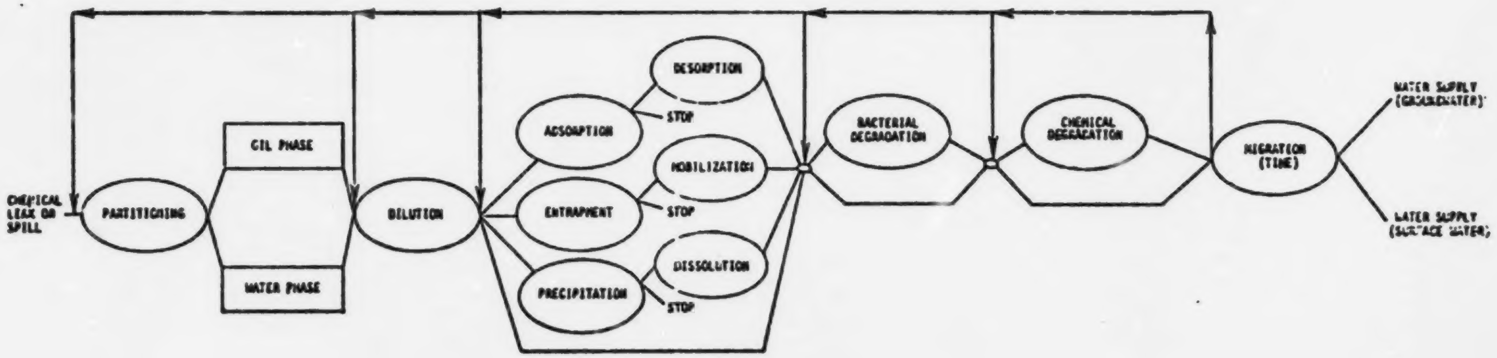
CHEMICAL LEAK OR SPILL
PARTITIONING
OIL PHASE
WATER PHASE
DILUTION
ADSORPTION
DESORPTION
STOP
ENTRAPMENT
MOBILIZATION
STOP
PRECIPITATION
DISSOLUTION
STOP
BACTERIAL DEGRADATION
CHEMICAL DEGRADATION
MIGRATION (TIME)
WATER SUPPLY (GROUNDWATER)
WATER SUPPLY (SURFACE WATER)

Figure 1-1. This figure shows that between the source of a spill or leak of chemicals used in tertiary oil recovery and a water supply there are a number of physical and chemical mechanisms which may act on the material.

1.1.2 Air Quality Conclusions

Widespread development of steam displacement projects to recover low gravity crude oils in shallow reservoirs could have a significant impact on air quality. The limits on sulfur content in fuels set forth in some state implementation plans are not adequate to prevent regional standards for sulfur dioxide from being exceeded. Table 1-2 illustrates the impact of a "typical" large recovery project. A variety of control strategies are available which may make it possible to keep regional air quality within the standards.

These strategies include advanced steam generator designs, installation of stacks, use of low sulfur fuels, combining emissions from several generators into one stack and flue gas desulfurization. Further analysis and dispersion modeling is required to assess the relative merits of each strategy.

The cost/benefit assessment of each of these strategies has a high priority for making environmental policy choices regarding tertiary oil recovery. The selection of required control strategies should consider the limitations imposed on the development of this petroleum resource and balance the benefits achieved with the reduction, if any, in the quantity of oil economically recoverable by steam displacement.

Air quality problems may also arise as a result of onsite manufacture of petroleum sulfonates. However, further research is required to characterize discharges, if any, from field-scale units and to identify needed control technologies for emissions as well as solid wastes.

Emissions from many sources in tertiary oil recovery projects have not been adequately characterized. It is important to consider reservoir characteristics and recovery process variables in the development of emission factors and the drafting of environmental policies to control pollutant discharges.

1.1.3 Recommendations

The thermal methods of tertiary oil recovery require early attention at the environmental regulatory level. In particular, new source performance standards need to be

TABLE 1-2

TERTIARY OIL RECOVERY

EMISSION REDUCTION REQUIRED TO MEET NATIONAL AMBIENT AIR QUALITY STANDARDS FOR FULL-SCALE DEVELOPMENT OF THERMAL RECOVERY FOR A "TYPICAL" LARGE FIELD IN INLAND CALIFORNIA[1]

(Base Case is burning 1 percent sulfur fuel oil, NSPS case assumes that the generators discharge not more than 0.8 pounds of sulfur dioxide per million Btu's)[2]

POLLUTANT STANDARD	MAXIMUM PREDICTED CONCENTRATION FROM THE FIELD ($\mu g/m^3$)		NATIONAL AMBIENT AIR QUALITY STANDARDS ($\mu g/m^3$)	POLLUTANT EMISSION REDUCTION TO MEET REGULATION (Percent)		MAXIMUM FUEL SULFUR CONTENT TO MEET STANDARD (Percent Weight)	
	Base Case	NSPS		Base Case	NSPS	Base Case	NSPS
Sulfur Dioxide							
Annual	140	(96)	80	43	(17)	0.57	(0.57)
24-Hour[a]	460	(315)	365	21	(--)	0.79	
3-Hour[a]	662	(452)	1,300	--	(--)	--	

[a] The 24-hour and 3-hour standards are not to be exceeded more than once a year.

[1] Typical large field is 9-section square (9 square miles) with uniform distribution of 36-20 MM Btu/hr and 72-50 MM Btu/hr steam generators with 4-meter and 6-meter vent heights respectively and no stacks, burning 1.23 percent sulfur fuel at 80 percent efficiency and 90 percent stream factor.

[2] At present there are no new source performance standards (NSPS) for oilfield steam generators.

developed for oilfield steam generators. EPA policy should support research to characterize discharges from tertiary oil recovery and monitoring of the types of chemicals planned for use in recovery processes in the future.

Unanswered questions regarding the possible environmental impacts of the other recovery processes should be addressed during the demonstration projects sponsored by the Energy Research and Development Administration (ERDA). Through cooperative EPA/ERDA research, environmental data should be obtained from such projects in sufficient detail so that variations in compositions of the discharges from tertiary oil recovery can be correlated over time with reservoir characteristics and process variables. The types of data which need to be collected are discussed below.

The following research areas are listed in order of recommended priority:

1. Cost/benefit analyses of air quality control strategies for thermal oil recovery projects assessing the levels of control attainable and oil reserves lost due to (1) exclusionary zones delineated by significant deterioration standards, and (2) shorter economic life of production as a result of the incremental costs associated with emission control.

2. Identification and prioritization of all point-and area-sources of hydrocarbon emissions in thermal oil recovery.

3. Characterization of and emissions factors for organic pollutants (particularly photochemically reactive species) from in-situ combustion and steam displacement as functions of process variables, reservoir parameters, time and oil characteristics.

4. Measurement of chemical concentrations in produced water from each of the processes, especially micellar-polymer flooding and in-situ combustion as functions of process variables, time, reservoir characteristics and oil composition.

5. Characterization of and emissions factors for inorganic pollutants such as oxides of sulfur and nitrogen from in-situ combustion as functions of process variables, reservoir parameters and oil characteristics.

1.2 Methodology and Scope of Report

The objective of this report is to set forth the potential environmental problems which may result from tertiary oil recovery processes. In this first-order analysis, statistics from the limited experience with tertiary oil recovery are used to extrapolate the problems that may occur during full-scale enhanced recovery. To date, field experience with the processes has been limited because of uncertain economic returns resulting from high costs and large technical uncertainties. Many processes which have been proposed remain untested, and there is insufficient field data on the others to readily determine the environmental impact of large-scale tertiary oil recovery on the basis of past activities. Where these data are unavailable, information from conventional petroleum extraction operations is employed. It is recognized that this approach may well overstate the future problems associated with tertiary oil recovery.

Therefore, as a preliminary environmental assessment of tertiary oil recovery, this report reviews the processes proposed in technical and patent literature as well as the state-of-the-art to identify areas of environmental concern which may require further quantitative definition and study.

1.2.1 Geographic Limits

The report is limited to oil fields amenable to tertiary oil recovery which are located on-shore within the "lower 48" states. While tertiary oil recovery may be carried out off-shore in some cases, lack of space on the platforms, logistical problems and other factors will generally preclude early development of tertiary oil recovery there. Primary and secondary recovery will be dominant in Alaska in the immediate future.

1.2.2 Problems Addressed

The focus of the study is upon those potential environmental problems which are unique to tertiary oil recovery as opposed to the environmental problems which have the same types and incidence as in conventional petroleum production operations. A comparative analysis of the industry's past performance in environmental protection was not within the scope of the effort. In addition to problems which may arise during the tertiary recovery activity, the report examines post-operational problems such as chemical degradation products and the failure of abandoned wells. The initial project scope encompassed potential water quality impacts and air quality impacts were included in this framework as the results of analysis became available. The report is organized in the following manner.

Chapter Two describes the processes, identifies the sources of possible environmental problems and indicates the process variables which may affect the magnitude of those problems at a given project site. In this chapter the following processes are examined (in order of emphasis): micellar-polymer flooding, steam displacement, in-situ combustion, miscible carbon dioxide injection. Dilute surfactant flooding and polymer flooding are discussed briefly as distinct techniques in comparison with micellar-polymer technology. Cyclic steam stimulation is included with the advanced thermal methods of oil recovery because it is sometimes used as part of a project applying these advanced techniques. Due to the shortage of natural gas and the present outlook for curtailed gas availability in the future, miscible hydrocarbon slug processes and miscible flue gas injection processes were not examined. The relative emphasis on the processes in Chapter Two is based upon the forecast potential for additional oil recovery by each technology.

Chapter Three examines the past and ongoing recovery activities and considers forecasts of future activity. Future recovery activities are assessed by process type and a rough first-order estimate is made of activities by process within regions of the country. Limits to the attainment of tertiary oil recovery forecasts are discussed.

Chapter Four presents details on the toxicity and carcinogenicity of chemicals which are proposed for use or which have been used for tertiary oil recovery operations.

Chapter Five develops some order-of-magnitude estimates of the probabilities that these chemicals will be released into groundwater and surface water systems as a result of well failure during or after tertiary oil recovery.

Chapter Six examines the impacts on air quality of enhanced oil recovery operations. Chapter Seven presents recommendations for further research and policy actions as indicated by the report.

1.3 Limits of the Analysis

The terms "tertiary oil recovery," "enhanced oil recovery," and "advanced oil recovery" are used interchangeably throughout this report. These terms refer to recovery of additional oil from fields which might have been produced by primary and conventional secondary means. In the case of low gravity oils these terms refer to production of oil which was technically or economically unrecoverable by conventional extraction methods.

The so-called tertiary oil recovery techniques may be most effectively utilized early in the life of an oil field rather than following other primary or secondary production techniques. Thus, the use of these methods could become much more widespread than estimated in Chapter Three. However, extended oil production from currently known domestic on-shore reservoirs is the most likely initial application of these techniques. In any case, these fields represent the largest potential for tertiary oil recovery. If the techniques are proven by extensive experience in the older fields, tertiary oil recovery projects in the fields of Alaska and off-shore may follow.

The application of tertiary oil recovery processes will depend upon a complex interaction of technical, political, and economic factors. The limits of this analysis of the potential environmental problems associated with the processes may also be grouped into technical, political and economic aspects. All of these factors may cause shifts in the relative importance of each process, the materials utilized, the level of activity, and therefore, the environmental problems which have been identified in the report.

1.3.1 Technical Factors

The technologies of tertiary oil recovery are in a phase of rapid evolution. New materials are being considered, and earlier concepts are being re-examined, and it is impossible to foresee what developments will arise in the future. As these processes evolve, the relative importance of different environmental problems may change.

Research is continuing to define the mechanisms which take place in the reservoir during tertiary recovery. This new knowledge will gradually supplant the differences of opinion which exist today regarding the functioning of the processes. Better technical understanding of the process mechanisms may provide a clearer insight into the environmental problems.

The reservoir data which is required to assess the feasibility of tertiary oil recovery is available only to a limited extent. The simple approach used here to identify the regional impact of tertiary oil recovery processes will need to be refined as better information becomes available. This review may result in interregional shifts in the types and amount of recovery activity.

1.3.2 Political Factors

Federal policies regarding energy sources, reduction in foreign supplies, petroleum pricing, incentives for application of new technologies, structure of the petroleum industry and environmental matters may affect the choices of recovery processes to be applied and the level of activity in tertiary recovery. To a lesser extent state and local regulations may influence the development and, hence, the environmental impacts of tertiary oil recovery.

1.3.3 Economic Factors

The limitations to development of tertiary oil recovery cited in Chapter Three are primarily economic. Chemicals and water supplies may not be available. Oil prices may not reach levels which are adequate to justify fieldwide programs. Excessive investment in redrilling and recompleting aged fields may sour the prospective returns. Conversely, in the case of chemicals, the demand for a paticular chemical may not be large enough to justify large-scale, efficient manufacturing units, thereby stifling the incentives to invest in needed capacity.

1.4 Research Needs

This study has sought to identify the potential environmental problems which may result from tertiary recovery. In many areas data are either lacking or incomplete with respect to environmental questions. Many of the answers may be sought in conjunction with the Energy Research and Development Administration field demonstration projects if environmental studies under EPA guidance are integrated into the demonstration programs. These research needs are:

- Characterization of and emissions factors for inorganic pollutants such as oxides of sulfur and nitrogen from in-situ combustion as functions of process variables, reservoir parameters and oil characteristics.
- Characterization of and emissions factors for organic pollutants (particularly photochemically reactive species) from in-situ combustion as functions of process variables, reservoir parameters, time and oil characteristics.
- Identification and prioritization of all point- and area-sources of hydrocarbon emissions in thermal oil recovery.
- Cost/benefit analyses of air quality control strategies for thermal oil recovery projects assessing the levels of control attainable and oil reserves lost due to (1) exclusionary zones delineated by significant deterioration standards, and (2) shorter economic life of production as a result of the incremental costs associated with emission control.
- Evaluation of field sulfonation processes for manufacture of petroleum sulfonates to assess environmental and economic impacts of processes.
- Evaluation of environmental impact of processes and chemicals used to treat oilfield production emulsions from tertiary recovery.
- Case studies and modelling of regional groundwater systems to assess the impact of well failure on water supply quality. The Chiquot formation in Texas is recommended as one of the areas for further study.

- Measurement of chemical concentrations in produced water from each of the processes, especially micellar-polymer flooding and in-situ combustion as functions of process variables, time, reservoir characteristics and oil composition.

- Assessment of environmental impact of a change in refinery loads to process and desulfurize a greater proportion of low gravity crude oils resulting from production by thermal methods.

- Quantification of the physical and chemical factors which may act upon leaks or spills of tertiary oil recovery chemicals. Define limits to degradation processes which may act upon chemicals used in tertiary recovery.

- Evaluation of the synergistic toxicity (plant and animal) and carcinogenicity of petroleum sulfonates and other materials.

CHAPTER TWO

TERTIARY OIL RECOVERY METHODS

2.0 Introduction

Initially, most oil fields have sufficient natural forces to push oil out of the oil-bearing rock and into the new wells. During this primary production phase, the advance of underground water beneath the oil may push it toward the well or natural gas dissolved in the crude may expand to force oil out of the rock much as champagne flows from an uncorked bottle. Producing naturally, a field may yield 20 to 30 percent of the original oil-in-place.[1] However, these natural forces are soon depleted and the oil production rate will drop sharply if secondary oil recovery techniques are not applied. In the secondary recovery phase the oilfield operator aids the natural pressure forces by injecting gas or flooding the oil reservoir with water. Unfortunately, the properties of the rock or oil in many oil fields preclude the enhancement of primary recovery methods. In appropriate cases, these measures may permit production of an additional 30 to 40 percent of the original oil in the reservoir. Today, nearly half of the domestic crude oil production of 3 billion barrels per year is obtained by secondary recovery. However, even oil fields that are most responsive under conventional primary and secondary recovery leave 30 to 40 percent of the original oil behind. New enhanced oil recovery techniques have been developed to solve a number of problems of conventional producing operations. These so-called tertiary recovery methods include thermal methods such as steam displacement and in-situ combustion, gas injection methods, and chemical methods. Thermal methods have been widely employed to reduce the viscosity of thick oils found in shallow California fields and elsewhere. Thermal recovery may account for 30 percent or more of tertiary oil production. Carbon dioxide and other gases have been tested. Injected into wells at high pressure, the gas mixes with oil and forces the oil ahead of it through porous rock more effectively than water. Approximately 20 percent of tertiary oil production may result from miscible gas injection. Chemicals have been injected to overcome the forces holding the oil in the rock and to improve the efficiency of waterflooding. Certain chemicals are used which "wash" the oil out of the reservoir rock the same way that laundry detergent acts on greasy stains.[1] Chemical techniques such as micellar-polymer flooding may produce about half of the recoverable tertiary oil. Each of these processes is described in terms of its inputs and its outputs and the efficiency and limitations of each method are analyzed. Appendix A is a glossary of some important technical terms used in tertiary oil recovery.

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[1] An average of 24 percent of the estimated original oil-in-place has been produced from the United States as of December 31, 1974. American Petroleum Institute, "Reserves of Crude Oil, Natural Gas Liquids and Natural Gas in the U.S. and Canada," May 29, 1975.

2.1 Micellar-Polymer Flooding

2.1.1 Introduction

In setting up waterflood projects, the field is drilled usually in a regular pattern consisting of a series of injection wells surrounded by production wells or vice versa. When water is injected into the formation, oil is driven toward the production wells where it is produced. Initially, the movement of oil is caused by the water pushing it through the formation. Following water breakthrough, however, the oil must be produced by being mechanically entrained in the water drive. Since oil and water are immiscible (they do not mix but rather form two phases), the water will tend to bypass oil which is trapped and held by capillary forces within the interstices of the formation. Only the oil which is within or directly adjacent to the flow paths of the water will be drawn into the fluid migration.

The technology of micellar-polymer flooding is similar in operation to a waterflood (although considerably more complicated), but it relies on chemical and physical forces to effect oil displacement. In a micellar flood, a "slug" containing a high concentration of surfactant is injected into the reservoir. The "slug" is called a micellar solution because the large concentration of surfactant causes the formation of micelles. One of the unique properties of an oil-external microemulsion is that it is miscible with the oil and, therefore, displaces the oil in the formation by dissolving it in the slug.

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[1] Shell Oil Company, Shell Reports -- Enhanced Recovery, (Houston, Tex., July 1975).

A second displacement mechanism, common to low tension floods (dilute surfactant) or to the leading edge of the micellar flood is related to the reduction of the interfacial tension between oil and water as a result of the presence of the surfactant in the micellar slug. As the interfacial tension is reduced, the capillary forces acting to hold the oil within the reservoir are reduced. When the interfacial tension is reduced to a very low value,[1] the capillary forces are no longer sufficient to retain the oil and, consequently, it flows freely out of the pores.

One of the operational problems relating to micellar-polymer flooding is that of mobility control. If the mobility of the injected fluid is significantly greater than that of the reservoir oil (as in the case of waterflooding), flow channels (fingering) will develop causing a significant portion of the oil to be bypassed. In the case of micellar flooding, the problem is even greater because the large difference between the slug and oil mobilities result in a rapid dispersion of the micellar slug, thereby reducing its effectiveness in displacing oil.

The environmental consequences of micellar-polymer flooding depend on the answers to the following questions:

1 What is the nature of the chemicals being used in this technology?

2. How much of each chemical is expected to be used at a given project as well as nationwide?

3. What is the final disposition of chemicals which are injected into an oil reservoir?

Although petroleum sulfonate surfactants may have a deleterious effect on water quality, none of the chemicals that are currently being used exhibit toxic or hazardous properties sufficiently severe to raise serious environmental concerns over present operations. A greater potential for environmental impact, however, may come from future developments. As the development of this technology proceeds, other chemicals will be developed which are less expensive, more effective, or more readily available. To be able to identify the environmental consequences of using these materials, specific toxicology data will be required. Many of the chemicals cited in the patent literature as being possible substitutes for the materials currently being used are discussed in Chapter Four regarding the hazards of tertiary oil recovery. Many other materials may be developed over the next several years, some of them hazardous and some of them not.

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[1] J.J. Taber found that it would be necessary to lower interfacial tension to about 10^{-3} dyne/cm to recover almost all of the residual oil. Society of Petroleum Engineers Journal 9(1) (1969).

The use of hazardous materials for enhanced oil recovery does not imply a direct environmental consequence. Rather, it suggests the existence of a potential threat of which EPA should be aware if it is to adequately assess the risks to the environment as opposed to the economic benefits to be gained by this technology.

The extent of any potential threat is, of course, difficult to assess, because there is very little published data on enhanced oil recovery and no hard fast rules governing the design of micellar flood projects. Within the scope of this preliminary assessment, however, it is important to attempt to quantify what the risks and hazards might be. To do this, first-order estimates are made of how much of each class of chemicals is used and where these chemicals go during "normal" recovery operations.

In the following sections a more detailed description of the physical mechanism governing micellar displacement of oil is given. The reader is cautioned that micellar-polymer flooding is still developing and differences of opinion concerning process details can be found throughout industry. In this work, representative numbers based on an analysis of published reports are presented. Although there may be some disagreement over the numbers presented in this and following chapters, the orders of magnitude of these numbers are intended to be representative of current technology which are of sufficient accuracy for this preliminary assessment of environmental consequences.

2.1.2 Oil Displacement Mechanism

The unique thing about oil-external microemulsions is that they achieve miscible displacement of the oil similar to the action of solvents on heavy grease. Consider for example, the ternary phase diagram shown in Figure 2-1. Each corner of the triangle represents a pure component in

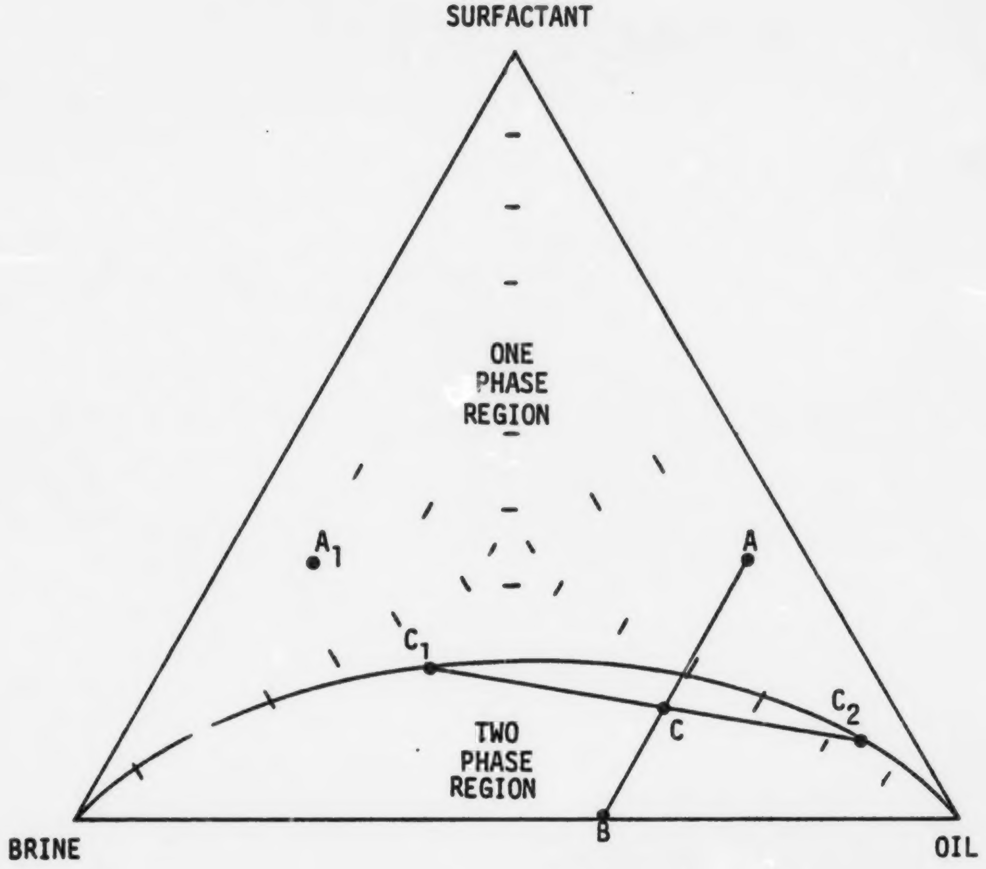
SURFACTANT
ONE PHASE REGION
A
A1
C1
C
C2
TWO PHASE REGION
BRINE
B
OIL

Figure 2-1. This ternary diagram illustrates the phase relationships which may exist when oil, brine and surfactant are combined.

a three-component system. The components shown are oil, water and the surfactant. The solid line on the ternary diagram separates the single phase region above and a two-phase region below. The unique property of this system is that for a wide range of compositions, a microemulsion forms such that oil and water co-exist in the single phase (i.e., they are miscible). In particular, a mixture of oil, water, and surfactant which forms a microemulsion would be miscible with oil found in a reaservoir. Therefore, the microemulsion would solubilize or dissolve the oil. Once solubilized, the oil would be incorporated with the microemulsion and driven toward the production well with the slug.

The process is actually more dynamic than described above in that:

1. The actual boundary between the one-phase and two-phase region depends upon the physical properties of the system such as temperature, pressure, the nature of the surfactant, the amount and nature of cosurfactant, the amount and nature of electrolyte, and perhaps a few other variables; and also
2. The micellar slug will change composition within the reservoir as oil and water are incorporated into the microemulsion or as adsorption of surfactant or cosurfactant occurs on the rocks and minerals.

Once the phase diagram for the system is known, the behavior of the slug within the reservoir becomes more predictable. For example, a micellar slug having the composition shown as point A on the ternary diagram (Figure 2-1). As the micellar slug mixes with the reservoir fluid shown as composition B in the diagram, the resulting composition of the mixtures falls along line AB on the diagram. Eventually, the composition of the micellar slug will be shifted into the two-phase region and will separate into a predominately oil phase and a predominately water phase. At this point, the micellar slug will no longer exhibit the miscible characteristics which allow the micellar solution to disolve the oil. However, oil will still be entrained in the mobilized fluids due to a reduction in the interfacial tension between reservoir oil and the surfactant-containing slug. Because the mobility of the predominately water phase is much greater than that of the oil phase, it will move more rapidly toward the production well leaving the oil phase behind to form an oil bank in front of the leading edge of the micellar slug.

In reality the physical chemistry of the surfactant/oil/brine system is considerably more complicated. The existence of many more than two phases within a single ternary system has been observed.[1] This is pointed out to caution the reader that actual systems are not nearly as simple nor as predictable as described above. However, this simple description is an adequate model for use in identifying environmental consequences of micellar flooding within the scope of this preliminary assessment.

2.1.3 Process Description

A typical micellar flood project proceeds in four distinct phases as shown schematically in Figure 2-2. They are:

1. Preflush which is injected into the reservoir to adjust salinity of the formation to be compatible with the optimum surfactant system. Final information on flow patterns may be obtained at this time. Chemical control of bacterial action may also be applied in this and subsequent steps in the process;
2. Micellar Solution (slug) including surfactant, cosurfactant, hydrocarbons, electrolytes, which in combination accomplish the miscible displacement of oil from the formations;
3. Mobility Control Solution (buffer), a low salinity water/polymer solution used to uniformly push the micellar slug through the formation in as close to a piston-like flow as possible; and
4. Water drive which pushes the micellar slug and mobility buffer through the reservoir to the production well.

Each of these steps is discussed below.

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[1] R.N. Healy and R.L. Reed, "Physicochemical Aspects of Microemulsion Flooding," Society of Petroleum Engineers Journal 10 (1974): 337.

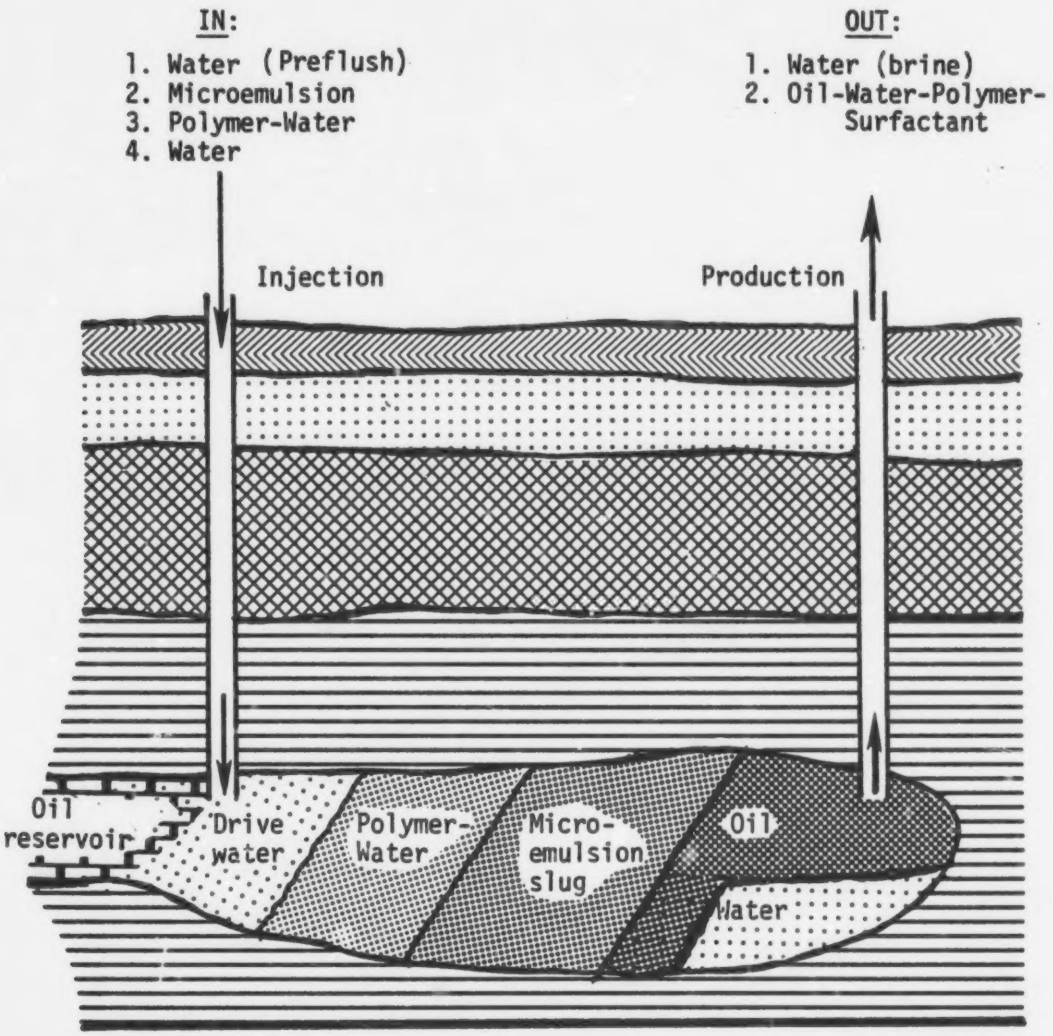
IN:
1. Water (Preflush)
2. Microemulsion
3. Polymer-Water
4. Water
OUT:
1. Water (brine)
2. Oil-Water-Polymer-Surfactant
Injection
Production
Oil reservoir
Drive water
Polymer-Water
Micro-emulsion slug
Oil
Water

Figure 2-2. This figure illustrates the micellar-polymer flooding process.

2.1.3.1 Preflush

In preparation for a micellar flood, the reservoir engineer must be concerned with how the slug and buffer solution will move through the reservoir. Selection of the surfactant system that will be most appropriate for the reservoir being flooded is also of concern. Initially, core samples are studied to determine the optimum micellar system which may include cosurfactant and electrolyte. Once this is known, a brine solution having the optimum concentration of electrolyte is injected into the well to (1) provide a tracer analysis of the project flow characteristics, (2) to adjust salinity if necessary, and (3) to reduce the concentration of divalent ions in the reservoir which may adversely affect the slug. In the presence of a high concentration of these divalent ions, the surfactant in the slug quickly loses its effectiveness through complexing or through formation of precipitates within the reservoir. Adsorption on selective ions within the reservoir clays has also been a problem.

2.1.3.2 Micellar Solution (slug)

At this stage in the development of micellar-polymer flooding, the design of the surfactant system for a particular reservoir is still very much an empirical art. The slug is composed of hydrocarbon, brine and surfactant. A cosurfactant, such as alcohol, and salts are also added to control stability and viscosity of the fluid. All of these compounds will have an effect on the system phase diagram.

In Table 2-1, typical recipes for microemulsions are given. The surfactant systems are generally classed as either low- or high-water and oil-external or water-external. Such a classification system is used more for convenience than for providing a chemical description of the microemulsion system. For example, a given surfactant could be used to form both oil-external and water-external emulsions depending upon the concentrations of brine and hydrocarbon included in the initial mixture.[1] In the ternary diagram shown in Figure 2-1, the mixture represented by point A is

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[1] Healy and Reed, "Physicochemical Aspects," 1974.

TABLE 2-1

TERTIARY OIL RECOVERY

SOME TYPICAL MICROEMULSION COMPOSITIONS[a,b]

CONSTITUENT	VOLUME PERCENT			
	LOW WATER[c] OIL EXTERNAL	HIGH WATER[d] OIL EXTERNAL	HIGH WATER[d] WATER EXTERNAL	LOW WATER[c] WATER EXTERNAL
Surfactant	6 - 10	3 - 6	3 - 5	6 - 12
Cosurfactant	2 - 4	0.01 - 20	0.01 - 20	3 - 25
Hydrocarbon	30 - 80	4 - 40	2 - 50	20 - 60
Electrolyte	0.001 - 5[e]	0.001 - 4[e]	0.001 - 4[e]	3 - 5[e]
Water	5 - 55	55 - 80	30 - 95	25 - 40

[a] W.B. Bleakley, Oil & Gas Journal 69(48) (1971): 50.

[b] Private communication, Union Oil of California, January 13, 1976.

[c] A "low water" emulsion slug is comprised of less than approximately 50 percent water. Some operators believe that such slugs are not economically feasible.

[d] A "high water" emulsion slug is comprised of more than approximately 50 percent water.

an oil-external emulsion. If, however, the proportion of brine to oil is changed leaving the amount of surfactant constant, the resulting mixture shown as point A_1 forms a water-external micellar solution. When the micellar solution is mixed with oil and brine within the reservoir, to the point that the composition becomes that shown as point C, the slug will separate into two phases -- one shown as point C-1 (a water-external emulsion) and the other shown as point C-2 (an oil-external emulsion).

The choice of surfactant and cosurfactant depends upon cost and flood design. Economic considerations usually restrict the choice of surfactant to petroleum sulfonates and the choice of cosurfactants to light alcohols. Natural petroleum sulfonates used for most micellar floods have a distribution of equivalent weights and will not be single compounds. Petroleum sulfonates with equivalent weight greater than 400 grams are predominantly oil-soluble and those with equivalent weights of less than about 400 grams are predominantly water soluble microemulsions.

The hydrocarbon in the slug may be crude oil produced earlier at the field (lease crude), gasoline, or kerosene, among others. However, lease crude is generally chosen because of its availability, low cost, and high compatibility with the reservoir.

2.1.3.3 Mobility Control Solution and Water Drive

A mobility control solution is required to push the microemulsion slug through the reservoir. Polymer is added to water to increase the viscosity of the mobility control solution. The solution exhibits unique flow properties. At high linear flow rates, such as occur near the injection well, the polymer solution gives low resistence to flow while at low linear flow rates further from the injector it gives high resistance to flow. The high resistance to flow causes the polymer solution to invade a larger portion of the reservoir and move through the reservoir more uniformly than water alone would do. A properly chosen polymer solution will force the microemulsion ahead evenly to contact a large part of the reservoir. The ratio of the part of the reservoir contacted to the total reservoir volume is known as the "sweep" efficiency of the micellar-polymer flood. In field operations a sweep efficiency of up to 75 percent has been achieved. The polymer used in a mobility buffer may also "plug off" parts of the oil reservoir by adsorbing onto the sand grains. Polyacrylamides exert mobility control by both methods. Polyethyleneoxides and polysaccharides only change the viscosity of the mobility buffer.

The concentration of polymer in solution is gradually decreased as the injection of the mobility buffer progresses. This has helped to improve the economics of micellar-polymer flooding because less polymer can be used overall and the process can then be completed by water injection. Polymer consumption will average about one pound per barrel of oil produced by the project. Very low concentrations of the polymer will appear in the produced water because of either adsorption or dilution.

When a polymer solution is injected alone and not in combination with a micellar slug, polymer concentrations will be evident in every barrel of water produced.[1] However, this has not been observed in field operations to date. The use of polymer solutions in this manner is not expected to have as widespread application as micellar-polymer flooding.

2.1.4 Process Efficiency

The efficiency of micellar-polymer flooding is dependent upon a complexity of factors. Among the most important variables are how much of the oil in the rock actually comes into contact with the surfactant in the slug and how evenly the mobility buffer pushes the oil and slug throughout the reservoir. Although there is a growing body of knowledge on the principles of micellar-polymer flooding, and the process may result in recovery of substantial additional quantities of oil from known fields, models to predict reliably the performance in various reservoirs are still under development.

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[1] Calgon Corporation, Bulletin 14-100, p. 12. Regardless of permeability, polymer was contained in the first drop oil produced water. At 600 ppm concentration of polymer in the injected slug, initial concentrations of polymer in the effluent were 300 ppm. (Results of laboratory studies in triple layer sand packs performed by Calgon Corporation to assess polymer retention.)

Many of the early laboratory studies bear little resemblance to the field results because improper scaling or oversimplification of the reservoir have so changed the parameters of the experiment that no comparison is possible. Many combinations of chemicals for micellar solutions have yet to be studied in the field. In view of these considerations, and the face that much of the required reservoir information has not been measured so that the reservoirs may be evaluated, it is nearly impossible to predict performance of micellar-polymer solutions with any quantitative accuracy.

The difficulty of predicting micellar-polymer flooding efficiencies has been one factor which has hindered wide-scale adoption of this method of oil recovery. Considering the large number of parameters which affect micellar-polymer flooding, qualitative estimates of the efficiency of the process can be made on the basis of important field characteristics. For a given oil saturation, the quality of injection water and the dissolved solids concentrations in the reservoir brine is an important characteristic. Table 2-2 lists a typical range of reservoir conditions which are suitable for micellar-polymer flooding.

Table 2-3 illustrates the efficiency of micellar-polymer flooding for different water quality conditions in reservoirs where the other important parameters are favorable. The highest efficiencies of recovery are achieved when the total dissolved solids and divalent ion concentrations in both the formation water and the injection water are low. Poor quality water within the formation may be overcome by preflushing the formation with injection water of high quality, and good efficiencies of recovery are possible. Fair to poor efficiencies of recovery are achieved when the quality of injection water is low due to high concentrations of total dissolved solids and divalent ions. Injection water problems in this case can sometimes be overcome by constituting the micellar slug with a higher proportion of hydrocarbon or by counteracting the adverse effects of the dissolved chemicals through chemical treatment. When the quality of injection water and the formation water are low, in terms of dissolved chemical concentrations, poor recovery efficiencies can be expected, and, in such cases, a fieldwide micellar-polymer flood would not be attempted.

TABLE 2-2

TERTIARY OIL RECOVERY

TYPICAL OPERATING RANGE OF IMPORTANT TECHNICAL PARAMETERS FOR MICELLAR-POLYMER FLOODING[a]

Oil viscosity	30 centipoise or less
Reservoir temperature	up to 200° F
Permeability[b]	more than 20-50 millidarcies
Total dissolved solids in brine[c]	less than 50,000 mg/L
Divalent ions in brine or reservoir clays[d]	less than 500 mg/L

[a] Factors such as oil saturation and porosity influence the economic feasibility of the process and laboratory studies are necessary to determine the affect of these parameters on technical feasibility.

[b] The ratio of variation in permeability should be less than 7 to 1.

[c] Mr. Geffen's original limit of 5,000 mg/L has been raised as a result of further research.

[d] Divalent ions which are typically found in oil field waters are calcium, magnesium, barium and strontium.

Source: T.M. Geffen, Amoco Production Company, "Improved Oil Recovery Expectations When Applying Available Technology," API Division of Production meeting, Denver, Colorado, April 9-11, 1973.

TABLE 2-3

TERTIARY OIL RECOVERY

EFFICIENCY OF MICELLAR-POLYMER FLOODING (GIVEN OTHER PARAMETERS ARE FAVORABLE)

		QUALITY OF FORMATION WATER (PREFLUSH OR FLOOD)	
		HIGH	LOW
QUALITY OF INJECTION WATER	HIGH	I EXCELLENT	II GOOD
	LOW	III FAIR TO POOR	IV POOR

Low Quality = Total Dissolved Solids > 50,000 mg/L
and Divalent Ions > 500 mg/L

High Quality = Total Dissolved Solids < 50,000 mg/L
and Divalent Ions < 500 mg/L

Recovery Efficiency = Percent of oil-in-place in the reservoir before tertiary recovery is started which is produced by the flood. Actual recovery efficiency in a given reservoir will also be influenced by the remaining oil saturation and other factors.

RECOVERY EFFICIENCY	0%	25	50	75
	POOR	FAIR	GOOD	EXCELLENT

2.1.5 Adsorption, Partitioning and Dilution

The answer to the question, "Where do all the chemicals go during a micellar flood project?", depends upon the following mechanisms:

1. Retention -- adsorption or entrapment of chemicals in the rock formation;
2. Partitioning -- the distribution of produced chemicals between the oil and aqueous phases;
3. Dilution -- the lowering of chemical concen tration due to a mixing with reservoir fluids.

2.1.5.1 Adsorption

In the ideal system, only the amount of surfactant necessary to produce a miscible microemulsion would be injected. Except for considerations of critical micellar concentrations, experimental work has not been published to indicate the minimum amount of surfactant required per barrel of oil recovered. In reality, additional surfactant is injected to account for material adsorbed onto the reservoir rock and clays. Since it is difficult to estimate in-site adsorption, at least some surfactant remains when the slug eventually reaches the production wells. At the present time, the amount of surfactant injected into the well is largely dependent upon adsorption characteristics of the reservoir formation. As the extensive development of new surfactants continues, several new formulations may be developed which would substantially reduce adsorption, thereby reducing the amount of surfactant used in the process.

To quantify the amount of surfactant adsorbed within the reservoir, the following data were considered. Trushenski reported adsorption data of a range of 0.5 to 2.0 pounds per barrel of pore volume in a preflushed Berea sand stone, core and range of 1.0 to 3.0 pounds per barrel of pore volume in a core which was not preflushed.[1] Gilliland reported data in the same range with some samples at high alcohol to surfactant ratios approaching an adsorption of zero.[2]

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[1] S.P. Trushenski et al., Society of Petroleum Engineers Paper 4582, 48th SPE meeting, (Las Vegas, Nevada, 1973).

[2] Gilliland, 9th World Petroleum Conference, Panel 14, Tokyo, Japan, May 1975.

Gale reported adsorption of approximately 1.4 pounds per barrel of pore volume, also in agreement with the above sources.[1]

2.1.5.2 Partitioning

The chemicals injected into the reservoir which are not retained by adsorption or other forms of retention, will eventually be produced when the oil bank and oil water emulsion reach the production wells. Surfactants and cosurfactants will be found in both the oil and water phases. A partitioning coefficient has been defined as the ratio of the weight fraction of chemicals found in the oil phase to the weight fraction of those found in the aqueous phase. In particular, the partitioning coefficient ranges from 0.1 and 1.5 for a sodium sulfonate with an equivalent weight of 427.[2] The partitioning coefficient varied with both the surfactant and cosurfactant concentrations and the surfactant-to-alcohol ratio. In addition, the alcohol partitioning coefficient for an unidentified alcohol was shown to be constant at approximately 0.5 over the same range of concentrations and sulfonate ratios as tested for the sulfonate partition coefficient.[3] In general, the partition factors will vary depending upon the surfactant composition and reservoir parameters. However, for this preliminary assessment, Gilliland's published data will be used as representative of typical partitioning to be expected.

2.1.5.3 Dilution

The environmental consequences of chemicals used in micellar flooding are often assessed in concentrations rather than in actual weight. Because the parameters of micellar flood vary widely, the concentrations of surfactant and cosurfactant found in the produced oil and water will also vary greatly. Even so, it is possible to make estimates of the concentrations that might be expected in the produced fluids based upon a consideration of the limited available data from existing micellar projects.

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[1] W.W. Gale and E.I. Sandvik, "Tertiary Surfactant Flooding: Petroleum Sulfonate Composition-Efficacy Studies," Society of Petroleum Engineers Journal, (August 1973).

[2] Gilliland, 9th World Conference, May 1975.

[3] Gilliland, 9th World Conference, May 1975.

The most difficult concentration to estimate is that of the surfactant in the produced oil and water since a considerable amount of the surfactant (if not all) is retained within the reservoir rather than being produced with the reservoir fluids. On the other hand, the cosurfactant such as alcohol are not expected to adsorb on to the formation because of its high water solubility. Instead, it will be retained in the formation only through entrapment. The remaining amount of cosurfactant will be produced with the reservoir fluids.

The total weight of surfactant and cosurfactant that is produced is the injected weight less the weight of material retained in the reservoir. When the slug materials are exposed to reservoir fluids and mixing occurs with the mobility control solution, these materials are diluted by oil or water depending upon the partitioning behavior of the compounds. The resulting concentrations of chemicals remaining in solution in the produced water, the reservoir water (and similarly, oil) will depend upon the recovery efficiency and oil saturation at the particular project. The weight (W) of these materials going into the oil is calculated from Equation 2-1; and the weight into water, from Equation 2-2. In the equations, P is the partitioning coefficient and R is the oil-to-water ratio of the produced fluid expressed in units of pounds of oil per pound of water.

$$W_{oil} = W_{total} \left[\frac{P(R)}{1+P(R)} \right] \qquad (2\text{-}1)$$

$$W_{water} = W_{total} \left[\frac{1}{1+P(R)} \right] \qquad (2\text{-}2)$$

The concentration in these two phases is then the weight of material divided by the volume. Using the knowledge of the micellar-polymer flood process and these mechanisms, the outputs of the process and material balances will be estimated in the following section.

2.1.6 Outputs of the Process

2.1.6.1 Water Consumption

Water is used in all phases of micellar-polymer oil recovery. The water carries chemicals into the formation, where they are left. Water produced by the process may carry some of these chemicals and plays an important role in diluting discharges of these chemicals to the environment.

Large volumes of water are used in preflushing, formulation of the micellar slug and the polymer solution, and in the follow-up water drive. For example, in some typical fields suitable for micellar-polymer flooding the following range in water usage might be expected. Table 2-4 illustrates estimated water consumption for various micellar-polymer flood situations. (Appendix B provides detailed data on the estimating procedure.)

As discussed earlier, when the connate water, or the water used in a previous waterflood, is not compatible with the micellar emulsion because of high ion concentrations, preflushing of the reservoir with water containing precipitating or neutralizing agents is necessary. Preflushing will use one to six barrels of high quality water per barrel of oil eventually recovered by the project.

Preparation of the micellar solution requires the use of water with concentrations of salts similar to those of the reservoir water or the preflush water. The water constitutes 30 to 95 percent by volume of the micellar slug, and thus, for this typical reservoir, from one-tenth to as much as two barrels of water would be required in the slug per barrel of oil to be recovered.

The mobility buffer consists of fresh water thickened with polymer. Its volume is usually about 50 percent of the total pore volume of the reservoir. The water requirement for the mobility buffer will be approximately two to five barrels of water per barrel of oil produced in most applications. An additional three or more barrels of water per barrel of oil produced are then required to complete the flood. Injection rates will vary with the permeability of the formation and the viscosity of the injected fluids. It is estimated that a micellar-polymer flooding project which requires a preflush could require as much as 19 barrels of water per barrel of oil produced of which up to 14 barrels of water must be of acceptably high quality.

TABLE 2-4

TERTIARY OIL REOCVERY

WATER CONSUMPTION IN MICELLAR-POLYMER FLOODING[a]

(Barrels water per barrel of oil produced)

		QUALITY OF FORMATION WATER[b] (BEFORE PREFLUSH)	
		HIGH	LOW
TYPE OF SLUG[c]	LOW WATER/ OIL EXTERNAL	6.5 - 9	8.5 - 12
	HIGH WATER/ WATER EXTERNAL	8.5 - 13	11.5 - 19

[a] Based on high quality water

[b] Low Quality, See Table 2-3
High Quality, See Table 2-3

[c] See Table 2-2 for definitions. For water consumption ~~estimates see Appendix B.~~

2.1.6.2 Chemical Consumption[1,2]

Surfactant usage will vary widely among projects even within the same region and geologic basin. The range of consumption can be expected to be 5 to 15 pounds of surfactant per barrel of oil produced in a micellar-polymer flood. Cosurfactant consumption may range from 2 to 10 pounds per barrel of tertiary oil produced. Polymer consumption will be approximately one pound per barrel of oil produced.

2.1.6.3 Reservoir Material Balance

From the information developed above it is possible to calculate an approximate material balance of micellar-polymer flooding in a typical reservoir. An example of such a calculation is shown in Table 2-5. The maximum injection rate of surfactant and cosurfactant is assumed to be about 15 pounds per barrel of oil and 10 pounds per barrel of oil respectively. Some of these chemicals will contact the reservoir but will not be produced with oil and brine due to entrapment or water breakthrough. A loss of 25 percent of these chemicals due to entrapment has been assumed in subsequent calculations. In addition, surfactants will be lost to the reservoir due to adsorption. At an adsorption rate of 2 pounds per barrel of pore volume, and an oil saturation of 50 percent, the actual rate of loss is 4 pounds per barrel of oil produced. Considering that the concentration of surfactant in the produced oil will approach zero when smaller quantities of surfactant are injected per barrel of oil ultimately produced, an adsorption curve such as the one shown in Figure 2-3 may be constituted.

The concentrations shown in Table 2-5 represent the maximum possible concentrations based upon the assumptions stated. Estimates based upon different assumptions will, of course, result in different estimates. For example, the effect of oil/water ratios is shown in Figure 2-4. At

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[1] C.F. Poettman cites the following example of chemical requirements per 100,000,000 barrels of microemulsion production which is developed: 1.7 billion pounds of surfactant, 7.24 million pounds of alcohol (18.1 million gallons at an average of 4 lb/gal), 102 million pounds of polymer (Petroleum Engineer 47 (1975): 42).

[2] Federal Energy Administration, Enhanced Oil Recovery Symposium, Washington, D.C., December 1974.

TABLE 2-5

TERTIARY OIL RECOVERY

EXAMPLE CALCULATION OF CHEMICAL CONCENTRATIONS IN PRODUCED FLUIDS

	SURFACTANT	COSURFACTANT
Maximum Injection Rates, Lb/Bbl of Oil	15.00	10.00
Loss from Sweep, 75% efficiency	3.75	2.50
Loss due to entrapment, 25% @ 50 percent saturation	4.00	-
Net Produced, Lb/Bbl of Oil	7.25	7.50
Partitioning (P_S=0.7, P_C=0.5, O/W=0.5)		
Oil Phase	1.88	1.50
Aqueous Phase	5.37	6.00
Concentration in Produced Fluids (ppm)		
Oil Phase	5,360	4,280
Aqueous Phase	7,660	8,550

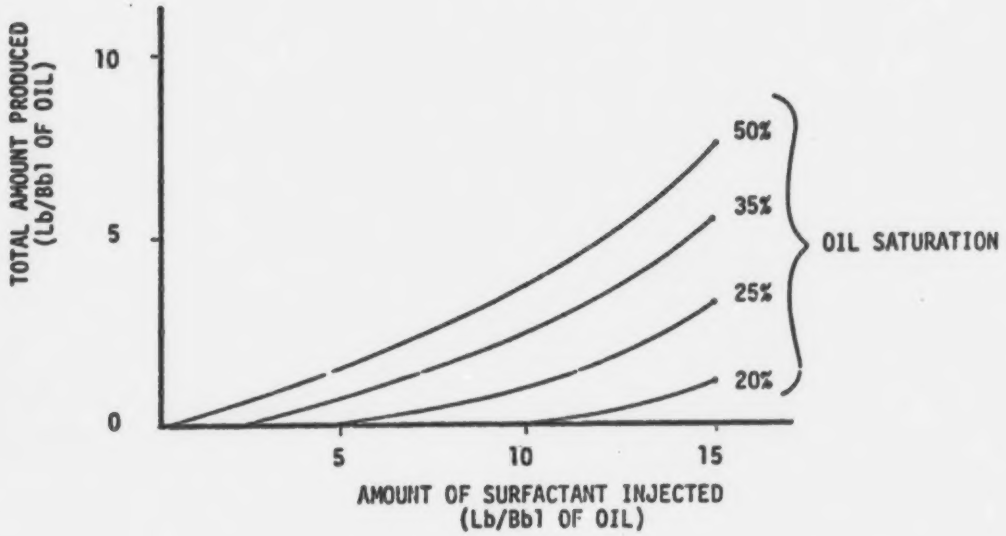

Figure 2-3. This figure shows that the amount of surfactant produced will vary with the amount of surfactant injected into the reservoir (based upon a maximum absorption of 2 Lb/Bbl Pv, 100 percent displacement efficiency, 75 percent sweep efficiency.

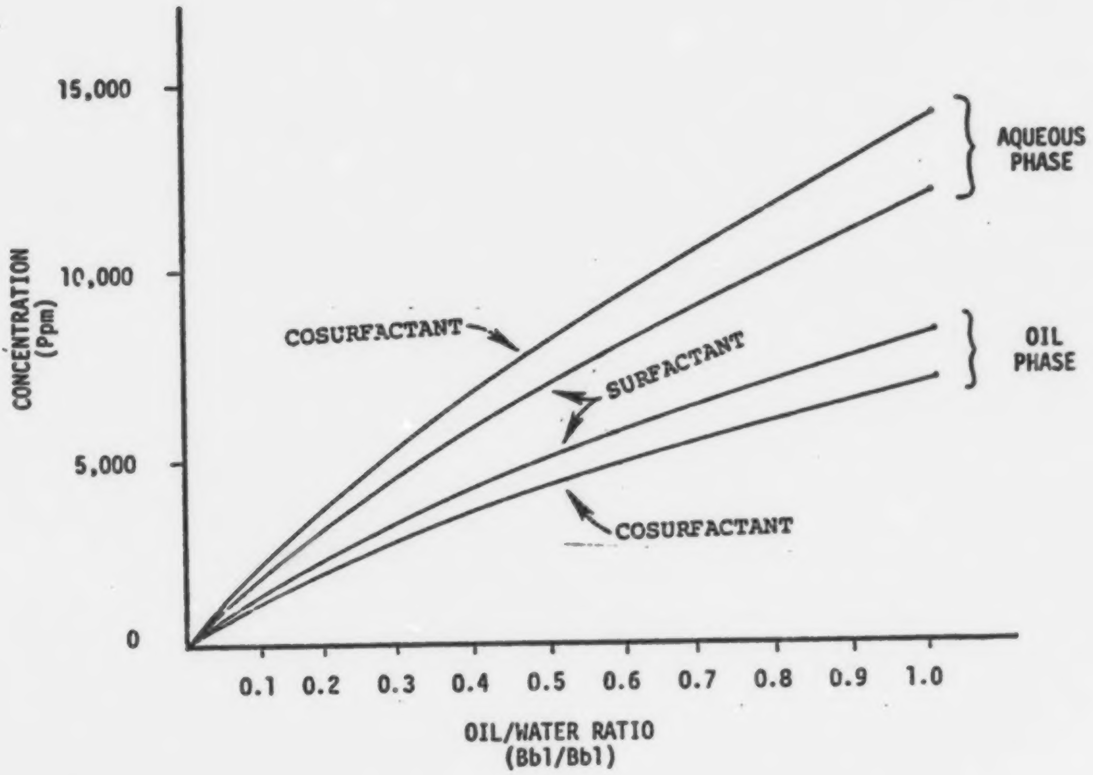

Figure 2-4. This figure shows that the concentration of surfactant and cosurfactant in the produced oil and water will vary with oil:water ratio of the produced fluid.

(Based on the following parameters)

	SURFACTANT	COSURFACTANT
Total weight (Lb/Bbl of Oil)	7.25	7.50
Partitioning Coefficient	0.7	0.5

relatively low oil/water ratios, the concentrations produced in the oil and aqueous phases are expected to be much lower than those shown in Table 2-5. On the other hand, oil/water ratios as high as 1.0 barrels of oil per barrel of water would result in concentrations of surfactants and cosurfactants considerably higher than those shown in the table. In particular, note that if the micellar slug displaces oil in the ideal pistonlike fashion, the oil/water ratio will approach 1.0 rather than 0.5 as assumed in the example calculations. Hence, the assumptions on which the examples are based are believed to be representative of present practice and may, in fact, be somewhat conservative.

The chemical concentrations in the produced fluids will also depend upon the initial rate of injection in that the amount of produced chemicals increases as the injected quantity increases. This is illustrated in Figure 2-5 showing concentration as a function of total weight produced. The estimated concentrations shown previously in Table 2-5 are based upon a maximum injection rate of 15 pounds per barrel of oil. Injection rates less than this will result in correspondingly lower exit concentrations. Though limited published field data are available, one set of process tests had a maximum surfactant concentration of 1,000 parts per million in both the oil and water phases at breakthrough.[1] From this preliminary analysis, it appears that higher concentrations are likely in the effluent from future tests.

Figure 2-6 summarizes the overall material balance for a wide variety of possible outcomes based upon these analytical techniques.

2.1.6.4 Chemical Manufacturing

Manufacture of the chemicals required may create pollutant hazards. Although on-site manufacturing facilities would be subject to pollution control regulations, the remote location of these facilities, their scale and simplified operating procedures may result in a higher incidence of uncontrolled discharges. Enforcement of scattered facilities may be more difficult than intensified monitoring of an increased level of output at large chemical

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[1] C.F. Poettman, Petroleum Engineer, p. 39.

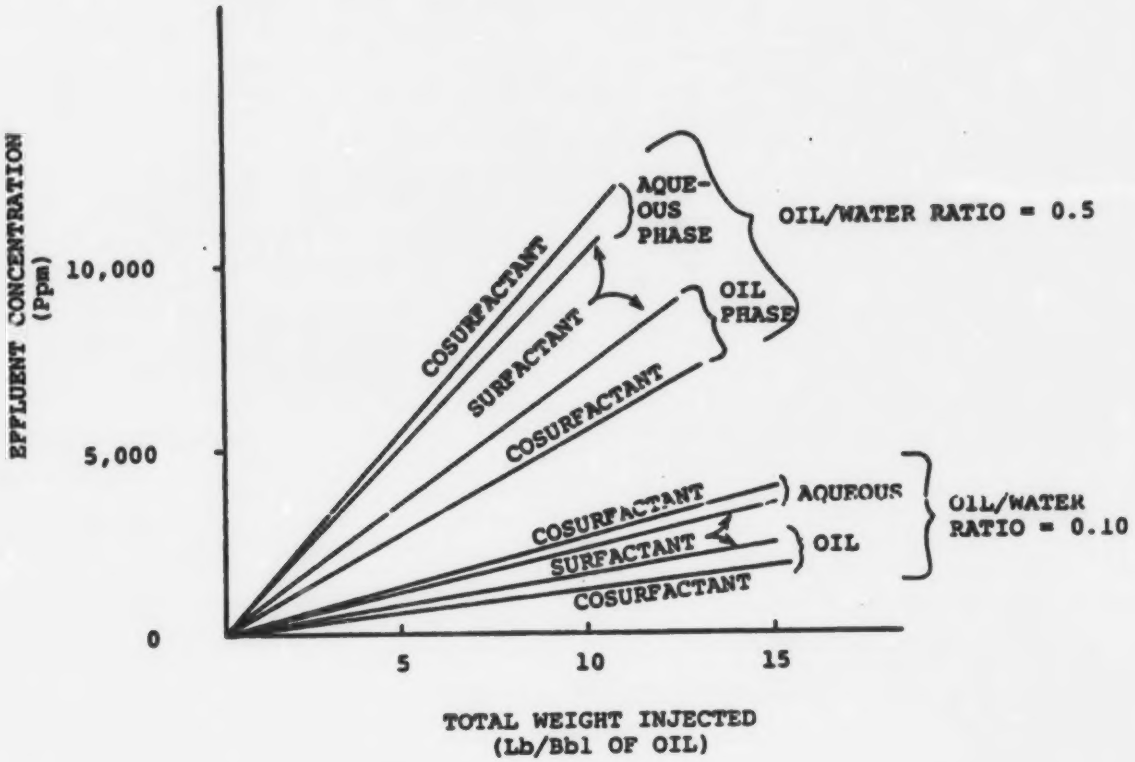

Figure 2-5. This figure shows the effluent stream concentrations of surfactant and cosurfactant for various injection quantities and two oil:water ratios. (Based on assumptions used in Table 2-5)

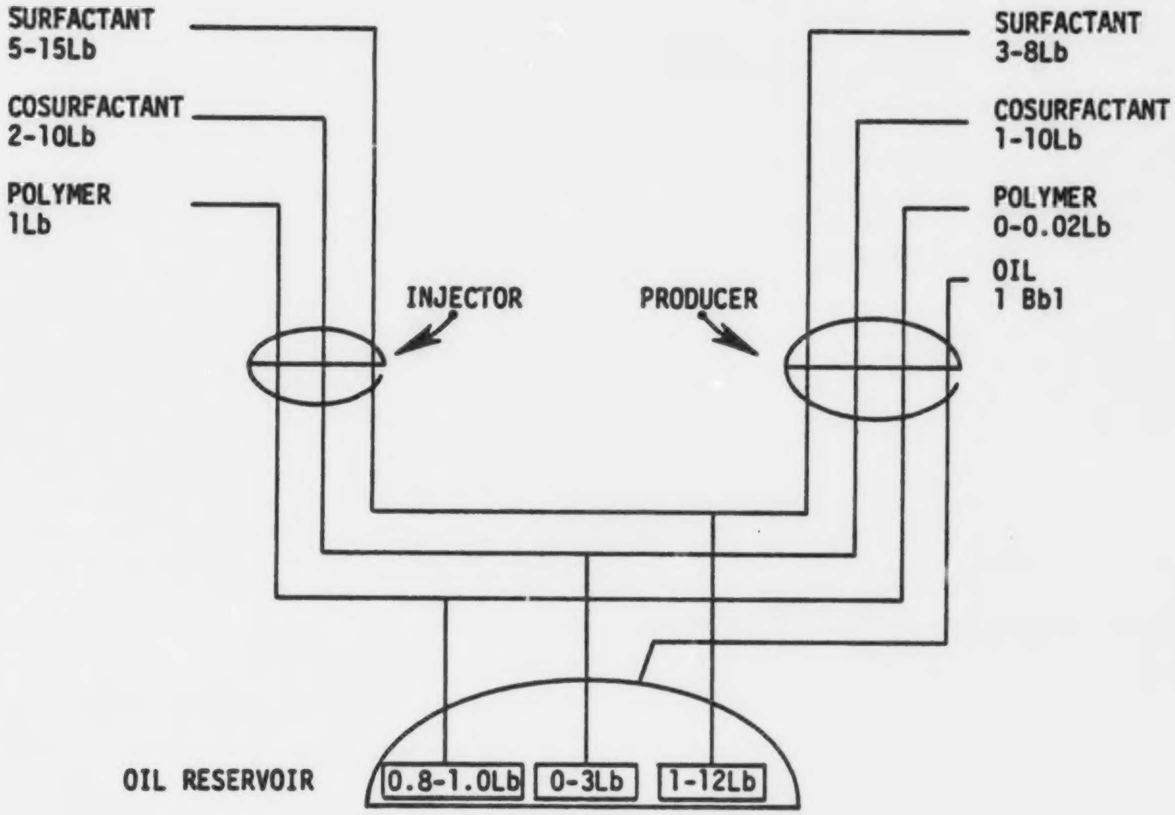
SURFACTANT
5-15Lb
COSURFACTANT
2-10Lb
POLYMER
1Lb
INJECTOR
PRODUCER
SURFACTANT
3-8Lb
COSURFACTANT
1-10Lb
POLYMER
0-0.02Lb
OIL
1 Bbl
OIL RESERVOIR
0.8-1.0Lb
0-3Lb
1-12Lb

Figure 2-6. This figure is the mass balance of chemicals used in a micellar-polymer flood. (Hydrocarbon in slug not shown for simplification of diagram.)

plants. The production of petroleum sulfonates may result in the emission of some unreacted gaseous sulfur dioxide and sulfur trioxide as well as a discharge of some sludge consisting of sulfonate complexes, sulfuric acid or sodium hydroxide and oil residue. Further studies of particular sulfonation processes are required to evaluate quantitatively the emission and discharge loads. These loads will vary regionally depending on the choices between field-scale and refinery-scale sulfonation.

2.1.6.5 Processing of Produced Fluids

The produced fluids from flood or surfactant flood are often emulsions which are difficult to treat economically in conventional oilfield separation systems. In order for the crude oil to be acceptable for refining it must contain less than 1 percent BSW (Bottoms, Settlings and Water) when it leaves the oil field. Higher water content in the crude oil would increase the refinery's energy usage (to boil off the excess water) and would also create problems of foaming, priming and corrosion. Conventional field treatment involves heating the produced oil and water or adding chemical deemulsifiers in concentrations of about 1 gallon of chemical per 10,000 barrels of oil (0.238 mm^3/liter). The most difficult emulsions from tertiary oil recovery production to date have required treating with dosages on the order of 1 pint of chemicals per barrel of oil (1.49×10^3 mm^3/liter). This huge increase in the volumes of chemicals used for treatment may introduce other potential environmental problems.

The presence of surfactants in the crude oil from tertiary oil recovery has not presented serious difficulties to refinery operations to date. A few changes in the operating conditions are all that is usually required to accommodate the materials. The amount of sulfur compounds normally added to the processes by the sulfonates is very small in relation to sulfur in most crudes.

2.2 Thermal Methods

2.2.1 Introduction

The tertiary oil recovery processes based on thermal methods improve oil recovery by two basic mechanisms. Since the processes have been tried primarily on more viscous crude oils, interest has focused upon reducing viscosity of oil in the formation to enable it to flow more easily toward the producing wells. In addition to viscosity changes, thermal methods increase oil recovery through some form of steam distillation of the oil in the formation. Other methods are involved, and the actual part played by each mechanism depends on the type of oil in the reservoir.

Two important methods of generating heat within the oil reservoir are of interest here: the injection of steam into the reservoir, and the burning of part of the oil in the reservoir by in-situ combustion of "fireflooding."

The important economic consideration for the thermal methods of tertiary oil recovery is the cost of fuel. Steam processes are sensitive to the cost of fuel required to generate the steam, whereas the important cost element in in in-situ combustion is the fuel required to power compressors which inject air into the formation. Similarly, most limitations to the thermal methods are based upon economic inefficiencies of heat loss rather than on technical factors such as reservoir chemistry. In particular, thin formations with low porosity are unfavorable for the thermal methods because too much heat is lost through the surfaces above and below the formations and it is too difficult to inject the steam or air into a tight formation without prior fracturing.

The environmental concerns of thermal methods arise from the generation of the heat and the effects of that heat on the produced fluids. Combustion products from steam generation and light hydrocarbon vapors from the distillation mechanism may be emitted to the air. Collection and recovery of hydrocarbon vapors is often economically justifiable and would be carried out by the prudent operator. However, fugitive emission problems may still exist. Chemical reactions may occur in the hot reservoir which create or release other compounds. These compounds may enter solution in reservoir water which may leak into groundwater systems.

2.2.2 Steam Injection Methods

Steam drive (or steamflooding) and cyclic steam soak (or huff-and-puff) are two common methods of steam injection. The oil recovery efficiency depends on the thermal properties and compositions of the reservoir fluid of the formation. Since the kinematic viscosity of the oil in the formation decreases linearly as temperature is increased, oil production is directly related to the temperatures achieved in the reservoir. The major technical limitation of steam processes is the depth of the oil-bearing strata. At greater depths, higher temperatures and pressures are needed for maximum effective usage of the steam. These operating conditions can cause damage to the well's casing and cement. The major factor contributing to inefficiency of steam injection processes is the loss of heat. Oil-bearing sands thinner than twenty feet are not favorable because too much heat escapes to rocks above and below. There is less loss of heat in the well when pumping into shallow formations. Surfact losses are on the order of 5 percent; wellbore heat losses may be in the range of 10 to 15 percent of the total number of British Thermal Units (Btu's) injected. Unfortunately, insulation is expensive and can only be justified for long-term projects.

2.2.2.1 Steamflooding

In this technique, steam serves to drive the oil as well as to reduce its viscosity. Steam is injected into the oil reservoir through injection wells. Separate production wells remove the oil.

The steam-saturated zone, in the reservoir whose temperature is approximately that of the injected steam, moves oil to the production well by steam distillation of the oil, solvent extraction, and a gas drive. As the steam cools and condenses a zone of hot water is formed which floods the formation. The relative importance of these mechanisms in the production of oil is shown on Table 2-6. Oil recovery efficiency ranges from 35 to 50 percent of the reservoir oil-in-place, depending on oil and reservoir characteristics.

TABLE 2-6

TERTIARY OIL RECOVERY

PERCENTAGE OF OIL PRODUCED PER MECHANISM IN A STEAM FLOOD

	TYPE OF CRUDE		
	NON DISTILLABLE	25% DISTILLABLE	50% DISTILLABLE
Hot water	87	75	68
Gas Drive	5	4	3.5
Distillation	0	14	22.5
Solvent Extraction	8	7	6
TOTAL	100	100	100

[1] Based on an analysis of laboratory data presented by B.T. Willman et al., Transactions of the AIME, 222, (1961) p. 681.

2.2.2.2 Cyclic Steam Stimulation

Cyclic steam stimulation enhances recovery by heating the remaining oil-in-place to reduce its viscosity, enabling it to flow toward the well. Steam is injected into the reservoir for a period extending from two to three weeks. The well is then shut in to allow heat to soak into the formation before allowing it to flow and later be pumped. The cycle is repeated once the oil production declines below an economically acceptable level. Though stimulated production may continue for up to six months, recovery levels will decline relatively soon. A yield of 20 to 35 percent of the oil-in-place is achieved, which is moderate in comparison to steamflood methods. This process is applicable to small oil pools as well as large reservoirs and has the advantage that continuous generation of steam for injection is not required.

A variation of these thermal methods, hot water flooding, has not been promising. This poor performance is attributed to a number of factors. The same capital investment in heat generating equipment is needed as in steam injection processes. Hence, the same environmental problems exist as for other methods which can achieve high recovery in a given field. Furthermore, wellbore heat losses are high -- up to 30 percent -- while overall heat loss has attained 60 percent. Oil recovery efficiency has been low -- generally, approximately 10 percent -- though in a few fields up to 20 percent of the remaining oil-in-place has been recovered.

2.2.2.3 Outputs from the Process

The emissions from oil field steam boilers depend on the size of the project, the oil recovery efficiency of the process, the heat losses which occur, with more than 100 boilers. Individual boilers range in size from 5 to 500 million Btu's per hour. One-third to one-fourth of the oil recovered is generally required for use as fuel and as reservoir production declines an economic limit is reached. Fuels for boilers may be natural gas, fuel oils, or crude oil from the lease. Though emissions will vary with the content of sulfur and other compounds in the crude, Table 2-7 illustrates the composition which may be expected in typical operations. To these emissions must be added the particulate discharge from boiler cleaning cycles and from trace metals in the crude oil fuel. Hydrocarbon may also be

TABLE 2- 7

TERTIARY OIL RECOVERY

EMISSIONS FACTORS FOR FUEL OIL COMBUSTION

(Pounds/1,000 Gallons of Fuel Oil Burned)[a]

POLLUTANTS	LARGE SOURCES (1,000 hp or more)	SMALL SOURCES (1,000 hp or less)
Aldehydes	1	1
Benzo(a)pyrene[b]	5,000 (μg/1,000 gal)	40,000 (μg/1,000 gal)
Carbon monoxide	3	4
Hydrocarbons	2	3
Nitrogen oxides as NO_2	105	40 to 80
Sulfur dioxide	157 S[c]	157 S[c]
Sulfur trioxide	2.0 S[c]	2 S[c]
Particulates[d]	8	23

[a] W.S. Smith, Atmospheric Emission from Fuel Oil Combustion, Public Health Service Publication No. 999-AP-2, R.A. Taft Sanitary Engineering Center, Cincinnati, Ohio, November 1962.

[b] Density of fuel oil equals 8 lb/gal, and 42 gal = 1 barrel.

[c] R.P. Hangebrauck, D.J. von Lehmden, and J.E. Meeker, "Emissions of Polynuclear Hydrocarbons and Other Pollutants from Heat-generation and Incineration Processes," Journal of the Air Pollution Control Association 14 (July 1964): 267.

[d] S = % sulfur in oil.

Source: U.S. Environmental Protection Agency, Compilation of Air Pollutant Emission Factors, August 1975.

released to the atmosphere at the wells during production. The particular operating and reservoir parameters of oil fields where steam displacement is carried out will determine the actual quantity of emissions.

2.2.3 In-Situ Combustion Methods

These tertiary recovery methods are based on generating heat in the formation by burning part of the oil there. Air is injected into the reservoir where ignition is induced by an electric heating unit or by spontaneous ignition of chemicals. The major costs of these methods are the capital and operating expenses of the equipment used to inject air in order to maintain the combustion process. As combustion advances in the reservoir, oil, lighter hydrocarbons, water and combustion gases are driven toward production wells.

Though fireflooding is applicable to a wide range of reservoir conditions, some oils do not form coke -- which is the fuel for the burn -- in adequate quantities. Asphaltic crudes, as a general rule, seem to burn better than paraffinic oils for a given gravity due to the former's high levels of bitumen. Peculiar characteristics within the oil-bearing strata also affect *in-situ* combustion. Some oils which leave high deposits of coking fuel could make the process uneconomic due to the large volume of air needed to maintain combustion. An increase in the rate of input of air produces higher combustion temperatures and therefore a higher efficiency. At a low air input, the percentage of the oxygen utilized is low and therefore the process is uneconomical because unnecessary costs are incurred in pumping air.

2.2.3.1 Process Description

A number of zones exist in the reservoir undergoing a "fireflood." In each of these zones, dynamic processes occur which determine the rate and amount of additional oil recovered. The burned region is composed primarily of clean, finely grained sand. The action takes place at the burning zone. Here, heat breaks down the oil into coke, which catches fire, and lighter oils are vaporized or move ahead of the burning region. Temperatures in this zone range from 600° F to 1,200° F depending upon the reservoir's physical characteristics and the operating conditions of the project.

Just ahead of the burning front is where coke is produced by craking and distillation of crude oil, which dissociates the lighter from the heavier hydrocarbons. The coke residual fractions are composed of high boiling point hydrocarbons containing oxygen, sulfur, nitrogen and trace metals. Molecular weights of these residual fractions range from 300 to 900 grams per mole. These fractions can represent up to 20 percent of the crude oil. Their exact composition is not known.

Another zone created in a fireflood consists of light hydrocarbons, which are vaporized by the burning front or other hot regions of the process. As the gases are driven through parts of the reservoir they displace some oil and improve the oil recovery.

An important variation of in-situ combustion method is a process known as wet combustion.[1] A fire is started in the formation. Then, water is injected alternatively with air to transfer excess heat from the burned region through and ahead of the combustion front in the form of water vapor. The effects of added heat and steam drive further reduce the viscosity of the oil ahead of the combustion front. With this process it is possible to move thicker oils than with a dry fireflood and to operate at lower pressures with possibly less fuel. Because less fuel may be burned, less air is required than with dry combustion. Though the process has not had wide application in the field, it is expected that recovery efficiency of 40 tc 60 percent of the original oil-in-place will be possible for mobile crudes and highly porous rock formations. Somewhat lower oil recovery efficiency (on the order of 30 to 50 percent) is expected where porosities and initial oil saturations are not as high.

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[1] One process of wet combustion known as COFCAW or "combination of forward combustion and waterflooding" has been patented by Amoco Production Company (formerly Pan American Oil Company).

2.2.3.2 Outputs of the Process

The high temperatures to which the reservoir is subjected in the burning region of a fireflood enable a number of chemical reactions to occur. The compounds created in this manner as well as the combustion residues may be present in the emissions at production wells. Others may be confined in the reservoir after the process is completed.

Possible emissions from an in-situ combustion project are varied. Some of the compounds listed in Table 2-8 may appear at the production wells. Table 2-8 is an analysis of the major constituents of the produced gas in a sample of thirty one in-situ combustion projects. No data on oxides of nitrogen or trace contaminants were developed, however. Light hydrocarbons, comprising 1 percent of the produced gas, appear chiefly as propane, methane and, to a lesser extent, ethane. Table 2-9 presents an estimate of the volumes of constituent gases produced per barrel of oil produced. Regional differences in the operating and reservoir characteristics of in-situ combustion projects would affect the emissions produced. The chemical and physical process of combustion within an oil-bearing stratum are complex and the possible environmental effects of combustion products need further study.

Sulfur compounds can be released in the burning of crude oils. Sulfur content of crude oils in the Wilmington area of California range from 1.7 to 2.5 percent below 17 degrees API gravity. For the purposes of this investigation, it was assumed that most of the sulfur compounds would remain in flood water or produced water during water combustion oil recovery processes. This assumption is based on the low pH of produced water from projects in the sample (a discussion of the chemistry is included in Appendix B). The typical values of pH were 2.7 to 4.0. The acidity of the water in the reservoir at the end of a fireflood could corrode the casings in plugged and abandoned wells and lead to contamination of aquifers.

Another source of potential contaminants is the residue of trace metals and metal oxides from the crude which may be dissolved by the acidic water left in the reservoir. Table 2-10 lists the concentration of trace elements in crude oils from various areas of the country. The residual fractions of the coke are not soluble in water, though trace metals may be dissolved by wet combustion process. Further research is required to assess this problem.

TABLE 2-8

TERTIARY OIL RECOVERY

COMPOSITION OF PRODUCED GAS STREAM FROM IN-SITU COMBUSTION[a]

(Percent Molecular Weight)

HYDROGEN		TRACE
Carbon Monoxide:		2.5 - 3.0
Carbon Dioxide:		12 - 14
Oxygen:		1.0
Nitrogen and Oxides:[b]		78 - 83
Hydrocarbons:		0 - 1%
(Methane	0.4-0.5)	
(Ethane	0.1)	
(Propane	0.4-0.5)	
pH of Produced Water:		1.6 - 8.6

[a] Based on a survey of 31 projects. These gas streams were measured at near optimum operating conditions early in the life of the flood. As the flood progresses the composition of emissions may change to include oxides of sulfur.

[b] Formation of NO_X compounds is not favored at the typical burning temperatures in a fire flood of 700-1,200° F. Most of the emissions would probably be nitrogen.

TABLE 2-9

TERTIARY OIL RECOVERY

AVERAGE EMISSIONS OF GASEOUS COMPOUNDS FROM IN-SITU COMBUSTION[a,b]

COMPOUND	EMISSIONS (Standard cubic feet per barrel of oil produced)
Carbon Dioxide	435
Carbon Monoxide	160
Nitrogen and NO_x [c]	4,220
Oxygen	185
Hydrocarbons	150

[a] Assumes all sulfur compounds remain in solution with produced water. However, emissions of SO_x may occur in the late phases of a fire flood.

[b] Based on a survey of the gas streams of 31 fire floods (average value).

[c] Formation of NO_x compounds is not favored at the typical burning temperatures in a fire flood of 700° F to 1,200° F. Most of the emissions would probably be nitrogen.

TABLE 2-10

TERTIARY OIL RECOVERY

TRACE ELEMENTS IN U.S. CRUDE OIL
(Parts per Million)

	ORIGIN OF CRUDE		
ELEMENT	CALIFORNIA	LOUISIANA	TEXAS
Antimony	<0.007	0.05	<0.01
Arsenic	<0.007	0.05	<0.12
Barium	<0.06	0.09	<0.14
Manganese	0.018	0.027	<0.05
Nickel	77	4.4	3.3
Tin	<0.6	0.5	<1.0
Vanadium	48	1	1.9

Source: E.M. Magee et al., Potential Pollutants in Fossil Fuels, EPA Report No. EPA-R2-73-249, June 1973.

Uncontrolled burning of oil reservoirs is not a problem in in-situ combustion. Electric heaters are often used to ignite the formation. Several cases of spontaneous ignition using air injection alone have been achieved in California and in the Woodbine formation in Texas. However, the fire is extinguished when air injection ceases.

2.3 Carbon Dioxide Methods

Though carbon dioxide is not completely miscible with most crude oils, it is soluble with both crude oil and water at reservoir temperatures and pressure. When carbon dioxide is injected and mixing occurs, the viscosity of the crude oil is reduced so that it flows more easily toward the production wells. Three variations are presently employed by the petroleum industry for tertiary oil recovery.

One method involves injection of carbon dioxide in a slug, followed by water or carbonated water. The second method involves injection of carbonated water directly. The third method involves injection of carbon dioxide at high pressures to achieve mixing directly with the reservoir oil and the formation of an oil-miscible slug in the formation. Though carbon dioxide reaches almost all of the oil in the reservoir and can achieve high contact efficiency with the oil, mobility control has been a continuing problem with the floods. Economic success of carbon dioxide methods is dependent on a nearby source of inexpensive carbon dioxide. Injecting carbon dioxide at high pressures is also expensive, as in the injection of air in in-situ combustion processes.

The major factors contributing to oil recovery in carbon dioxide flooding are formation of a miscible slug in in-situ modification of viscosity and changes in oil density and compressibility of fractions. By maintaining the slug in a single dense phase, its solubility with crude oil is increased considerably. Crude oil viscosities ranging from 5 to 90 centipoise can be reduced by a factor between 10 and 100 times under high injection pressures of carbon dioxide. After a carbon dioxide flood has been completed, the gas comes out of solution to some degree due to reduction in pressure, creating a further gas drive within the reservoir.

One problem that has also been noticed in the use of carbon dioxide injection processes is the effect of precipitation of asphalt compounds under carbon dioxide pressure. Variations in carbon dioxide flooding have been attempted which incorporate the use of foaming agents with the flood to achieve more mobility control with the gaseous medium. These techniques, however, have received few trials on a fieldwide basis to date.

2.3.1 Outputs of the Process

Carbonic acid is formed when carbon dioxide dissociates into the water in the reservoir. Operational problems of carbonic acid corrosion have been reduced by injecting water and carbon dioxide separately. Corrosion of casings may occur after the fluids reach the reservoir and are produced. Seepate of acidic fluids from wells at the recovery project could affect groundwater.

Safety in handling carbon dioxide and hydrogen sulfide is also required. On February 2, 1975, a gas leak occurred at a carbon dioxide injection well in Texas resulting in nine deaths by H_2S poisoning. To date this is the only such case recorded, yet it does suggest that such tragic accidents could occur along pipelines or at the wellsite. Control systems to detect leaks and limit the escape of carbon dioxide to small quantities are available and are required by regulation in some states.

CHAPTER THREE

THE PETROLEUM INDUSTRY AND TERTIARY OIL RECOVERY

3.0 Introduction

The environmental impacts, if any, of tertiary oil recovery projects are likely to increase or change as the amount of recovery activity increases in number and size in the future. To understand fully the scope of these impacts and to place them into a national context, the potential sites, the processes and the structure of the industry which will carry out this activity will be examined in this chapter.[1]

Although early tertiary recovery projects have been characterized by technical difficulty and financial risk, the potential of additional oil recovery has spurred the development of a number of operations. At least 32 companies have undertaken more than 200 advanced recovery projects in this country. Over 70 percent have been located in Texas or California, with the remainder in 13 other states. Of those undertaken, approximately 130 are currently active.

In addition to projects completed or underway, numerous others are being planned or have recently begun operation. In 1974 at least 22 enhanced recovery programs were scheduled to commence within the year, reflecting rapid increases in the price of international crude oil and continued interest in tertiary recovery. Thirteen others were slated for operation before 1980. By last year 14 companies had settled on plans for 35 projects in 12 states. Almost half were to be located in California, where thermal recovery methods have proven both feasible and profitable in unlocking low-gravity crude oils.

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[1] The following company-process analysis was developed from a sample of planned and ongoing sophisticated recovery projects contained in the March 25, 1974 issue of The Oil and Gas Journal supplemented with additional reports on Independent projects and programs supported by the Energy Research and Development Administration.

3.1 Current Operations

Because of the financial risks involved, major domestic crude oil producers dominate the tertiary recovery industry. The list of projects in Table 3-1 indicates a relatively high degree of industry concentration among the major oil companies. Table 3-1 shows that companies among the Top 20 initiated 80 percent of those projects undertaken before 1974; the Big Eight alone accounted for almost two-thirds.

To gauge more accurately the involvement of particular companies in tertiary oil recovery, it is necessary to separate the activities into pilot and fieldwide projects. Generally, fieldwide projects require a larger investment than pilot projects if research personnel costs are excluded. By this criterion, the larger companies appear more active. Roughly 60 percent of the projects operated by firms in the Top 20 are classed as fieldwide; for Big Eight firms the corresponding figure is 66 percent. Relatively fewer projects of the smaller firms -- 56 percent -- were dubbed fieldwide by their operators. The gap between the Big Eight and the smaller firms is initially non-existent for projects slated to begin in 1974 or subsequent years; both groups expected roughly 60 percent of these to be fieldwide. However, firms among the Top 20 but outside the Big Eight appear to have escalated their efforts in the area; fieldwide activities were slated for 70 percent of their new projects, indicating an increasing commitment to processes which have been proven on a pilot scale.

Cross-classification of tertiary recovery projects by process and location demonstrates an uneven distribution. For example, Texas -- with slightly over one-fourth of all projects -- has had a third of all combustion projects. Similarly, 62 percent of all miscible hydrocarbon and 75 percent of all miscible CO_2 sites have been located in Texas. California has had over 80 percent of all steam drive programs. Breakdowns of projects by location and method are found in Table 3-2. Figures 3-1, 3-2, and 3-3 pinpoint these project locations throughout the country. An unbalanced distribution characterizes the classification of projects by process and company. While experimenting with a variety of tertiary recovery methods, most firms appear to rely heavily on two or three. Although steam soak, combustion, steam drive and polymer flood are popular individually with many companies, each company is involved to a different extent in each method. Hence, regulations aimed at particular processes would unevenly affect companies within the industry.

TABLE 3-1

TERTIARY OIL RECOVERY PROJECTS FOR FIRMS AMONG THE TOP TWENTY

	OVERALL DOMESTIC PRODUCTION RANK[a]	TERTIARY RECOVERY RANK[b]	PROJECTS PLANNED	PROJECTS COMPLETED OR UNDERWAY	TOTAL PROJECTS
Exxon	1	11*	0	2	2
Texaco	2	3*	7	9	16
Gulf	3	6	1	10	11
Shell	4	7	0	10	10
Standard of California	5	2	4	16	20
ARCO	6	8	0	9	9
Amoco	7	5	0	14	14
Mobil	8	1	0	37	37
Getty	9	9*	6	2	8
Union	10	11*	0	2	2
Sun	11	9*	1	7	8
Conoco	12	3*	0	16	16
Marathon	13	10*	0	3	3
Phillips	14	10*	1	2	3
Cities	15	11*	1	1	2
Skelley	18	11*	1	1	2
TOTAL			22	141	163

[a] Based on the Federal Trade Commission Report released on July 18, 1973.

[b] Determined on the basis of projects planned and projects underway.

*Indicates more than one company in same risk.

TABLE 3-2

LOCATION OF TERTIARY OIL RECOVERY PROJECTS

	Calif.	Texas	Wy.	Ok.	La.	Ill.	Miss.	Ark.	Pa.	Col.	N.D.	Ind.	Ky.	Neb.	N. Mex	Kan.	TOTAL
Thermal																	
Combustion	12	15	1	3	7	1	2	2						1		1	45
Steam Soak	48																48
Steam Drive	26	1	1		2		1	2									33
Hot Waterflood				2													2
Subtotal Thermal	86	16	2	5	9	1	3	4						1			127
Chemical																	
Polymer Flood	1	12	5	3						1			1		1		24
Micellar Solution Flood		1	1	2	1	3			3		1				1		13
Surfactant Flood		2	1									1					4
Soluble Oil Flood		1				1											2
Caustic Soda Flood		2															2
Low Tension Water Flood																	
Subtotal Chemical	1	18	7	5	1	4			3	1	1	1	1		2		45
Gas																	
Miscible Hydrocarbon	5	13	2	1													21
Miscible CO_2		6					1			1							8
Waterflood/ Alternating Gas			3	1													4
Water/Gas Injection		1															2
Water/Gas Pulsing		1	1								1						2
Flue Gas							1										1
Subtotal Gas	5	21	6	2			2			1	1						38
TOTAL	92	55	15	12	10	5	5	4	3	2	2	1	1	1	1	2	211

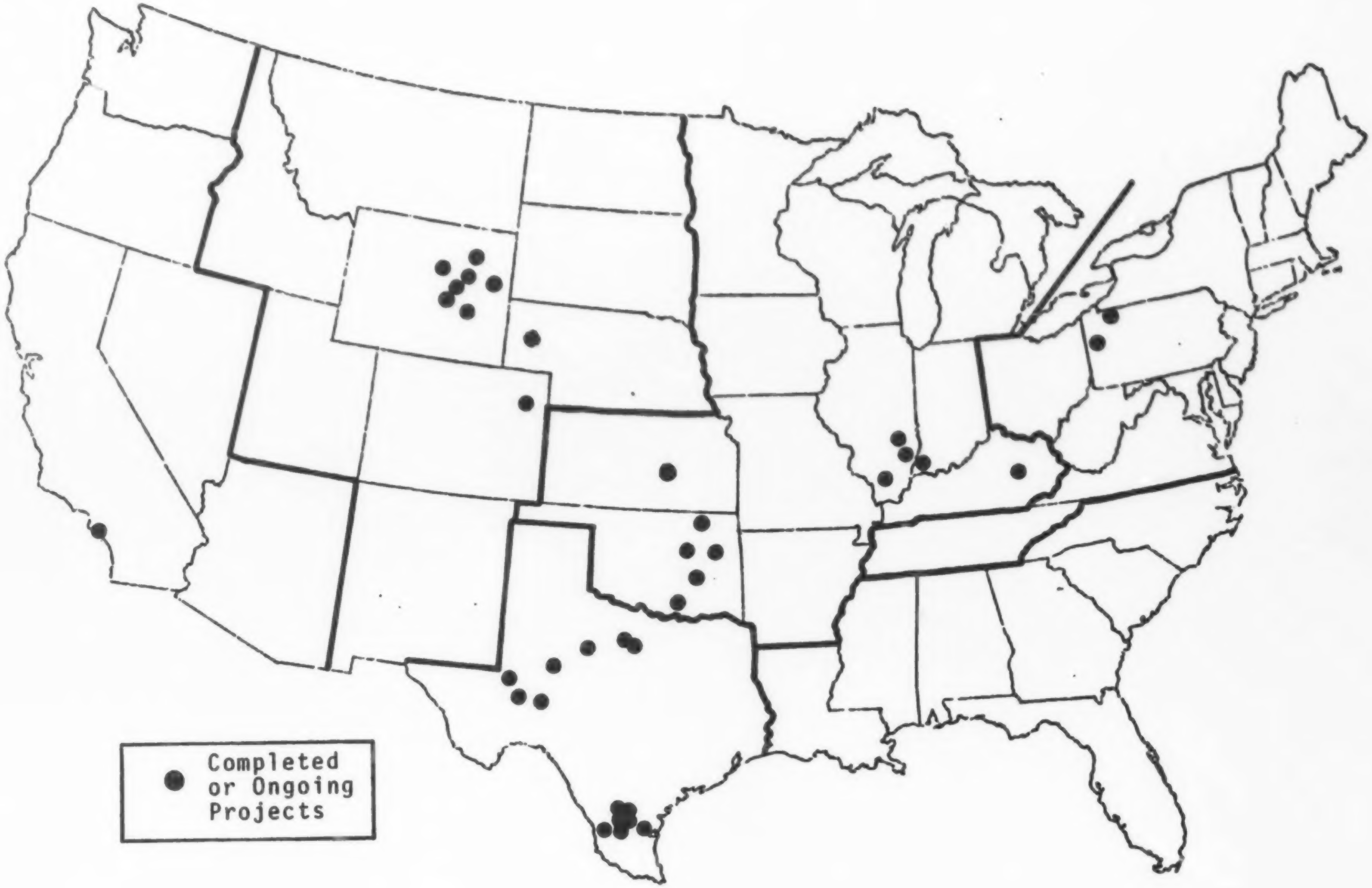

● Completed or Ongoing Projects

Figure 3-1. This figure illustrates the location of completed or ongoing chemical flooding projects.

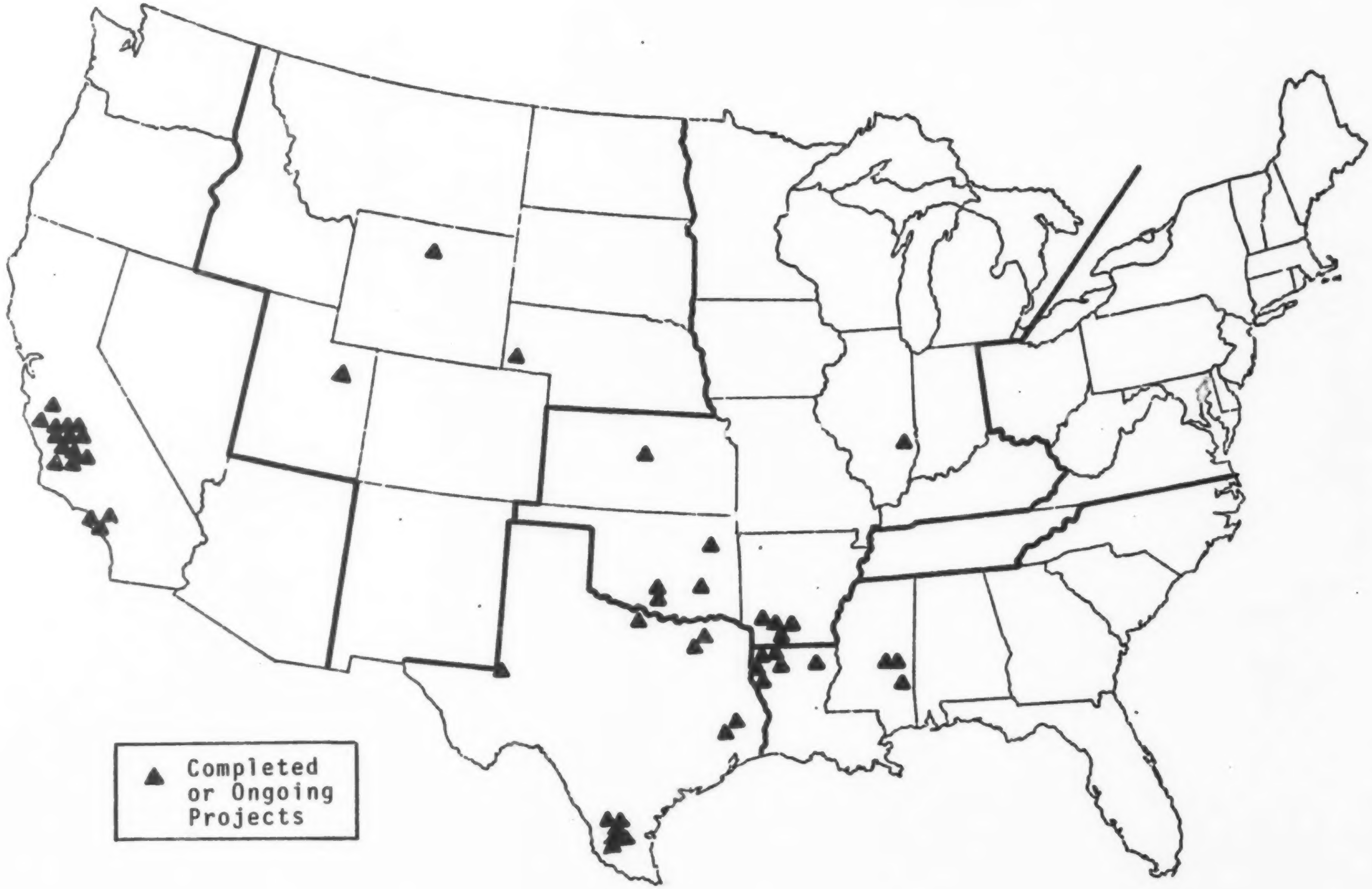

▲ Completed or Ongoing Projects

Figure 3-2. This figure illustrates the location of completed or ongoing thermal tertiary recovery projects.

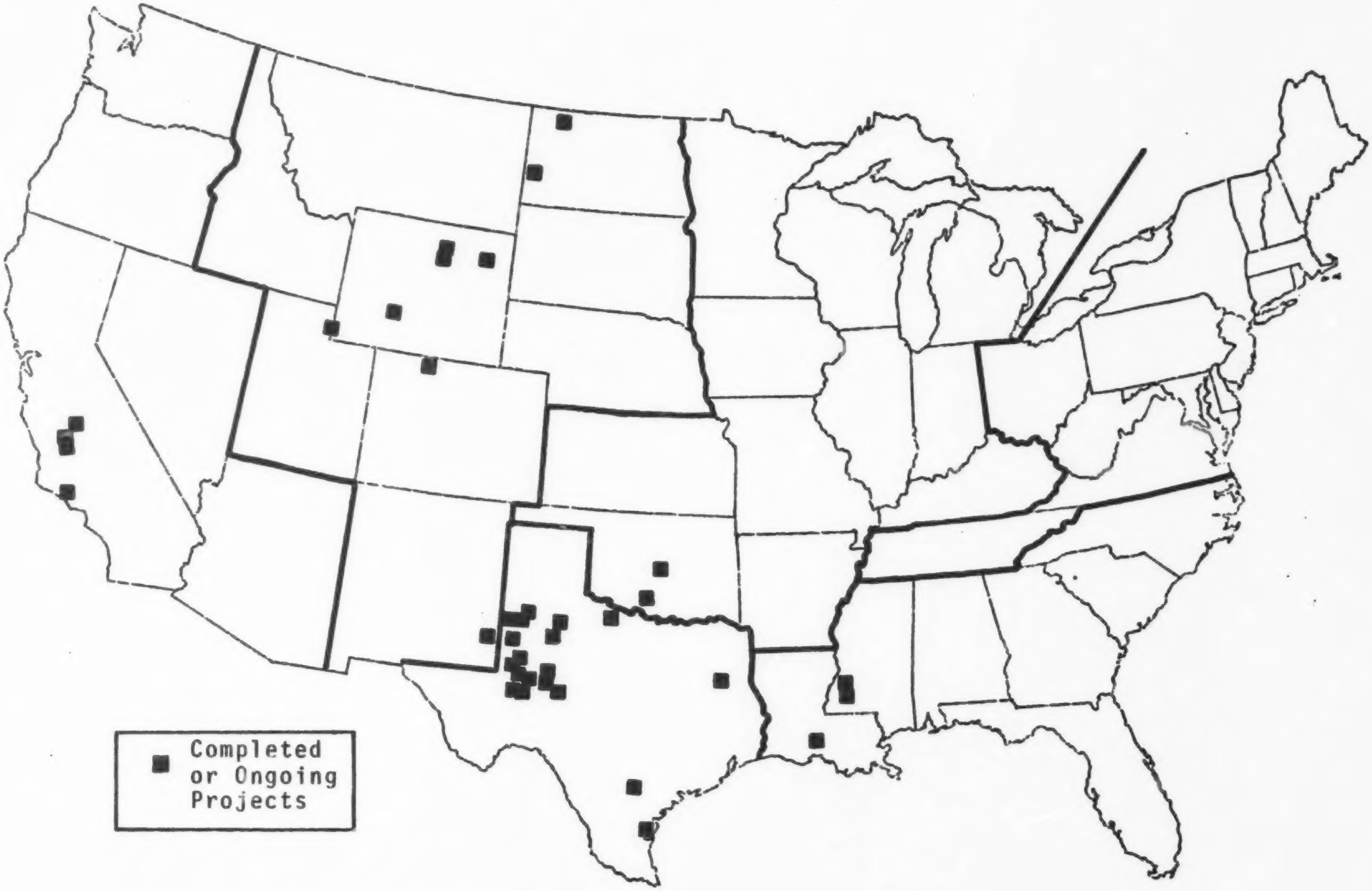

■ Completed or Ongoing Projects

Figure 3-3. This figure illustrates the location of completed or ongoing miscible-CO_2 injection projects.

The widespread popularity of certain processes may in part be explained by examining their respective profitability records. Evaluations of various methods from all companies undertaking enhanced recovery have been combined in Table 3-3 to yield a set of profitability ratios. Processes which have been proven and expanded to fieldwide operations generally have the best profitability ratios. Smaller companies appear to choose the proven processes for enhanced oil recovery whereas the Top 20 are more involved in demonstrating advanced techniques. Independents listed 71 percent of reporting projects as moneymakers, whereas the comparable figure for programs administered by companies within the Top 20 was only 55 percent. The ratios are likely to improve for many processes as operators learn more about the best prospects upon which to apply them. For example, in-situ combustion, having a profitability ratio of only 23 percent, was designated for six projects scheduled for 1974 or later. Other methods lacking substantial profitability data such as micellar solution flood and combinations of water and gas injection were also slated for the same period.

3.2 Future Prospects

These advanced oil recovery projects and new tests should provide the technical understanding necessary for tertiary oil recovery to expand on a larger scale. The fact that these technologies are still relatively young as regards fieldwide applications makes it difficult to extrapolate future oil production by tertiary methods from current activities. This is less of a problem for thermal methods than for micellar-polymer flooding as reflected in the disparity of estimates for its further potential. Adding still another estimate here of the recovery potential is not within the scope of this investigation and would only obscure the examination of other important issues. Instead, a critical appraisal of other forecasts will be made to select a basis for determining the environmental consequences of tertiary oil recovery.

3.2.1 Forecasts of Tertiary Oil Production

Recently, a number of estimates of the potential of tertiary oil recovery have been made (Table 3-4). There is obviously wide disagreement among the estimates resulting from the particular setting assumed in each forecast. The higher estimates may be considered to be overall targets for

TABLE 3-3

TERTIARY OIL RECOVERY

PROFITABILITY OF TERTIARY PROCESSES[a]

	# COMPLETED OR UNDERWAY	# REPORTING FINANCIAL STATUS	# PROFITABLE	PERCENT PROFITABLE
Combustion	39	30	7	23
Cyclic Steam	42	39	39	100
Steam Displacement	22	17	9	53
Polymer Flood	20	16	6	38
Miscible Hydrocarbon	21	18	13	72
Miscible CO_2	9	5	1	20
Micellar Solution Flood	7	1	1	0
Waterflood Alternating Gas	4	3	3	100
Surfactant Flood	4	2	0	0
Caustic Soda Flood	2	1	0	0
Hot Waterflood	2	2	0	0
Low Tension Waterflood	1	--	--	--
Soluble Oil Flood	1	1	0	0
Water/Gas Injection	1	1	1	100
Water/Gas Pulsing	1	1	0	0
TOTAL	176	137	80	

---

[a] Based on an analysis of data presented in the March 25, 1974 issue of The Oil and Gas Journal.

TABLE 3-4

FORECASTS OF TERTIARY OIL RECOVERY

(Billions of barrels)

SOURCE	LOW	HIGH
FEA[a]		65
NPC[b] Case I	11.4[c]	20[d]
GURC[e]	18.5	36.3
Mathematica[f,g]	7.0	16.0

[a] Federal Energy Administration, Review of Secondary/Tertiary Recovery of Crude Oil, 1974.

[b] National Petroleum Council, U.S. Energy Outlook Oil and Gas Availability, 1973.

[c] Production over next 15 years by tertiary recovery from old and new fields, excludes 18.5 billion barrels produced by secondary methods. Daily average production rate estimated at 1.79 million barrels by 1985 from tertiary methods.

[d] Reserve additions due to tertiary recovery projects over next 15 years.

[e] Gulf Universities Research Consortium, Planning Criteria Relative to a National RDT&E Program Directed to the Enhanced Recovery of Crude Oil and Natural Gas, November 30, 1973. Daily average production of 1.8 million barrels by tertiary recovery estimated in 1985.

[f] Mathematica, Inc., The Estimated Recovery Potential of Conventional Source Domestic Crude Oil, May 1975.

[g] Excluding "extended waterflooding" estimates of 8-9 billion barrels.

the future. But, in a shorter time frame, 65 billion barrels of output estimated by the Federal Energy Administration is probably not achievable in view of any reasonable combination of economic, political and technical developments. The additional production by tertiary methods which will occur during the coming 10 to 15 years is of most interest. During this transitional period a clearly formulated and soundly implemented set of Federal policies and regulations would permit the orderly development of tertiary oil production.

There is a greater variance in the forecasted proportional application of each type of recovery technology than in the total production estimates. Table 3-5 indicates the differences between the Mathematica and Gulf Universities Research Consortium (GURC) forecasts. The forecasts of cumulative oil production by recovery technique are compared in Table 3-6. An analysis of the Mathematica study reveals the causes for its pessimistic results.

While the "Big Oil Fields" file is as good a data base as can be compiled without access to information held by individual companies, Mathematica's forecasts of the potential of enhanced oil recovery suffer from deficiencies in the technical understanding of the recovery processes and reservoirs and in the use of the data file.

The major shortcoming of the study is its analysis of micellar-polymer flooding. Its costs are considered to be high and the potential additional recovery is estimated at only 250 million to 2.5 billion barrels. These discouraging conclusions were reached because the study views the technology statically. That micellar-polymer flooding is expensive today is indisputable. The process does not perform well on reservoirs with high permeability contrast or where high concentrations of divalent cations such as calcium, magnesium and barium exist in the rock matrix and in the connate water. However, if reservoir inhomogeneity and geochemistry do not pose insurmountable problems, a decrease in the costs of materials can be expected in the future through a learning-curve effect and economies of scale.

A panel of the petroleum industry's experts on enhanced oil recovery provided the GURC estimate that oil production by micellar-polymer flooding could reasonably exceed 21 billion barrels. Their estimate seems to take into account some of the technical advancement which should occur. The costs of earlier micellar-polymer flooding projects will be large, but such high costs are not projectable indefinitely into the future. These early costs are necessary in order

TABLE 3-5

TERTIARY OIL RECOVERY

PROPORTIONAL CONTRIBUTIONS OF RECOVERY METHODS

(Percent Total Tertiary Oil Recovery)

	RECOVERY METHOD		
FORECAST SOURCE	MISCELLAR-POLYMER	THERMAL	MISCIBLE CO_2
Mathematica[a]	3-16[c]	61	23-36
GURC[b]	58	29	13[c]

[a] Mathematica, Inc., The Estimated Recovery Potential of Conventional Source Domestic Crude Oil, May 1975.

[b] Gulf Universities Research Consortium, Planning Criteria Relative to a National RDT&E Program Directed to the Enhanced Recovery of Crude Oil and Natural Gas, November 30, 1973.

[c] Includes negligible amount by miscible hydrocarbon.

TABLE 3-6

TERTIARY OIL RECOVERY

FORECASTS OF TOTAL OIL PRODUCTION BY RECOVERY METHOD

(Billions of barrels)

	MATHEMATICA		GURC	
RECOVERY METHOD	LOW	HIGH	LOW	HIGH
Micellar-Polymer	0.25[c]	2.50[c]	9.2	21.1
Thermal	4.25	9.75	4.6	10.5
Miscible CO_2	2.50	3.75	2.0[d]	4.7[d]
Total	7.0	16.0	15.8	36.3

[a] "Assured" - as captioned in report.

[b] "Reasonable" - as captioned in report.

[c] Includes miscible hydrocarbon recovery method.

[d] Includes miscible hydrocarbon recovery method.

to establish the reserves as a recoverable national resource. Of course, even higher levels of recovery may be achieved given a suitable economic climate, focused incentives and developed technology.

Despite its shortcomings, the Mathematica study will be used as a lower value for tertiary oil production. The GURC forecast of "reasonable" production will be considered to be the upper limit for the period through 1985-1990. Thus, the production of 7 to 36 billion barrels of oil by tertiary recovery methods can be expected during the transitional period when the rate of development and growth will be highest.

3.2.2 Development and Growth

The actual rates of development and growth of tertiary oil recovery projects will depend upon the interplay of economic, political and technical factors. Other considerations may create further differences in the development rates among regions of the country. However, given the potential oil production as forecasted, the growth of tertiary recovery in each region can be evaluated by identifying: (1) the locations of oil fields in each region in which a project appears feasible, and (2) particular limitations to growth which predate these advanced recovery methods.

3.2.2.1 Location of Technically Feasible Projects

The locations of the known oil fields in the United States are shown in Figures 3-4, 3-5, and 3-6. Texas and Southern-Central California are mapped separately to provide better definition of detail. Six regions of the country are identified -- Pacific West, Rocky Mountains, South Central, North Central, Southeastern and Northeastern. These regions were selected on the basis of the API Reserve Subcommittee geographic districts with some minor modifications.

The potential sites for tertiary oil recovery projects were chosen using the methodology described in Appendix B. For each type of recovery method the project sites have been outlined in Figures 3-7 to 3-15.

Figures 3-7 to 3-9 show that micellar-polymer flooding projects are most common in Texas. The North Central and South Central regions also have a significant number of

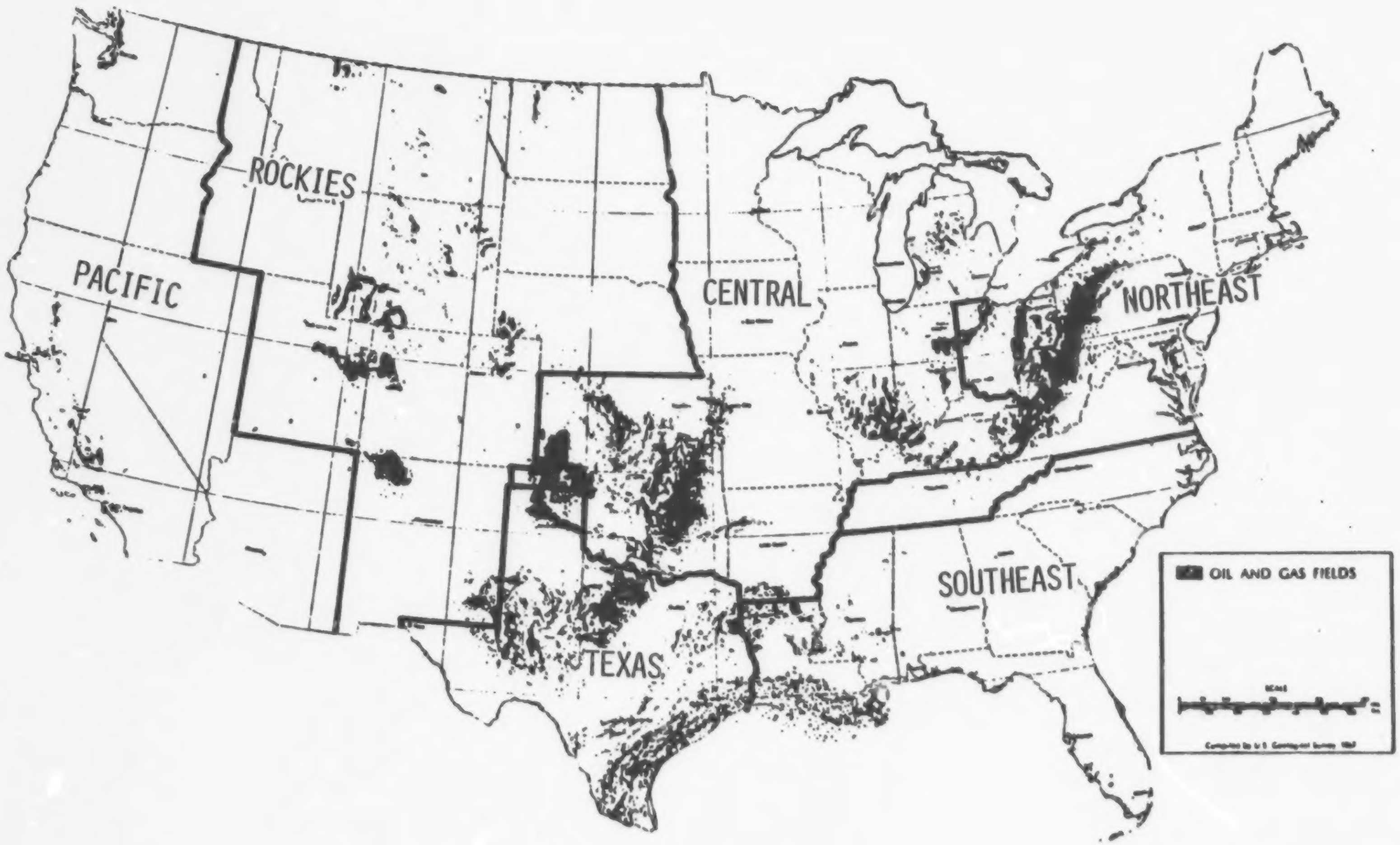

ROCKIES
PACIFIC
CENTRAL
NORTHEAST
TEXAS
SOUTHEAST
▨ OIL AND GAS FIELDS
SCALE

Figure 3-4. This figure gives the location of oil and gas fields in Continental United States.

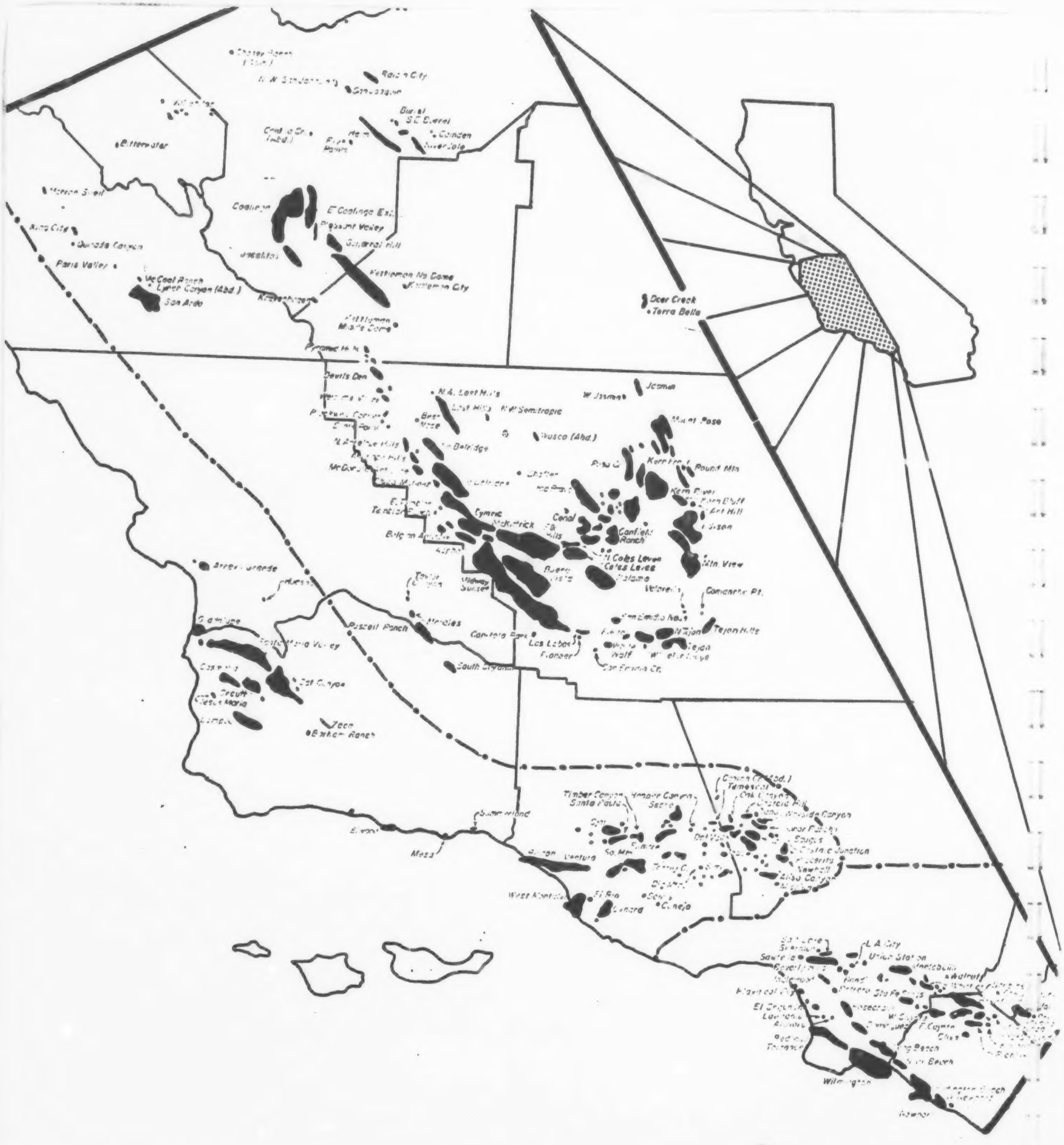

Raisin City
Burrel
S.E. Burrel
Camden
Riverdale
Bitterwater
Coalinga
E. Coalinga Ext.
Pleasant Valley
Guijarral Hill
Kettleman N. Dome
Kettleman City
King City
Quinado Canyon
Paris Valley
McCool Ranch
Lynch Canyon (Abd.)
San Ardo
Deer Creek
Terra Bella
Devils Den
N.A. Lost Hills
Lost Hills
N.W. Semitropic
Belridge
W. Jasmin
Jasmin
Mount Poso
Round Mtn
Kern River
Kern Bluff
Cymric
McKittrick
Canal
Canfield Ranch
Coles Levee
Buena Vista
Midway Sunset
Mtn. View
Comanche Pt.
Tejon Hills
Los Lobos
Pioneer
Wheeler Ridge
San Emidio Cr.
Russell Ranch
South Cuyama
Arroyo Grande
Guadalupe
Santa Maria Valley
Casmalia
Cat Canyon
Orcutt
Jesus Maria
Lompoc
Zaca
Barham Ranch
Summerland
Ellwood
Mesa
Timber Canyon
Santa Paula
Hopper Canyon
Sespe
Temescal
Oak Canyon
Saugus
Castaic Junction
Newhall
Aliso Canyon
Ventura
So. Mtn.
West Montalvo
El Rio
Oxnard
Conejo
L.A. City
Union Station
El Segundo
Torrance
Wilmington
Long Beach
Seal Beach
Newport

Figure 3-5. This figure illustrates the location of oil fields in Southern California.

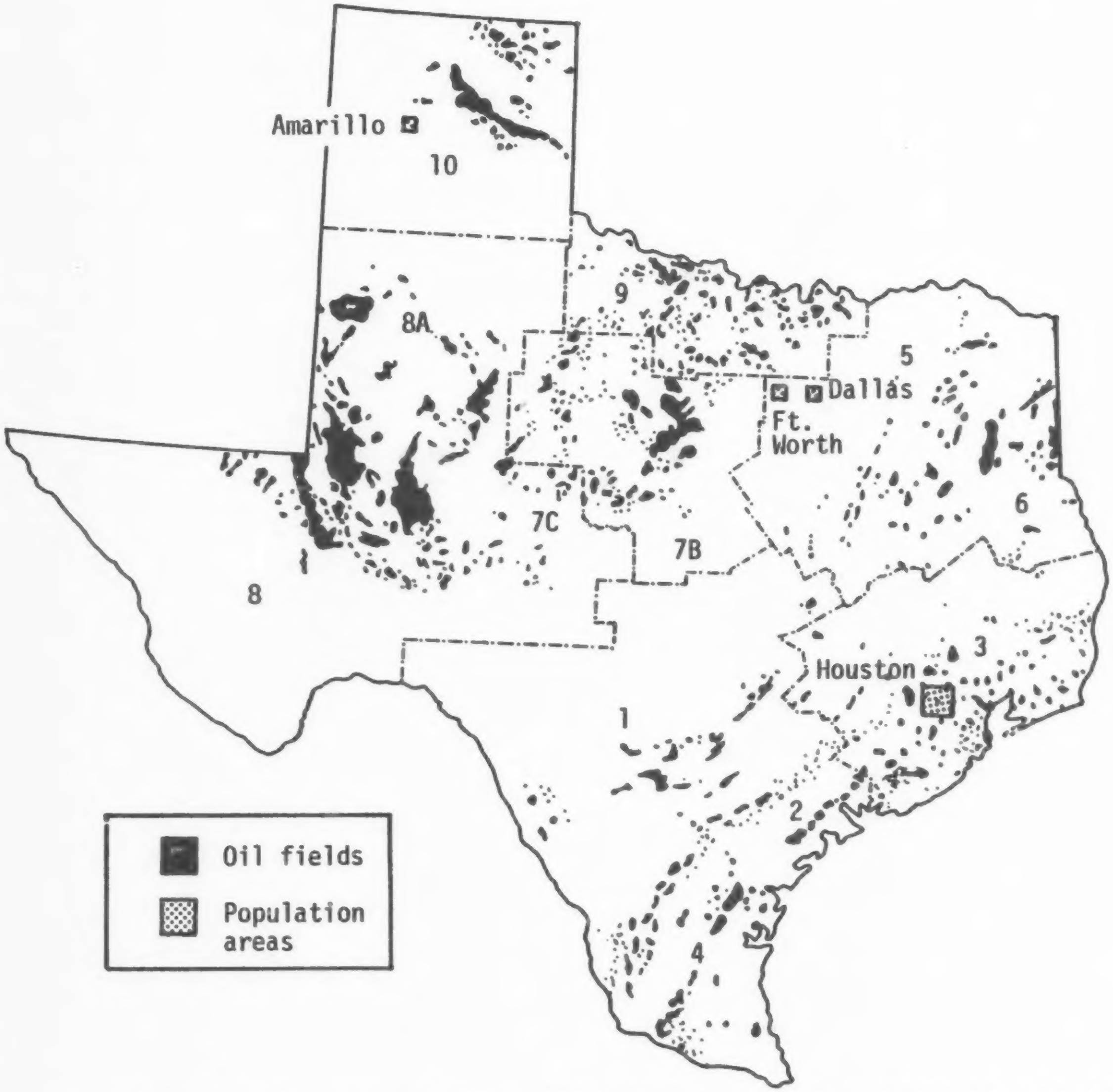

Amarillo
10
9
8A
5
Dallas
Ft. Worth
6
7C
7B
8
Houston
3
1
2
4
Oil fields
Population areas

Figure 3-6. This figure illustrates the location of oil fields in Texas Railroad Commission Districts.

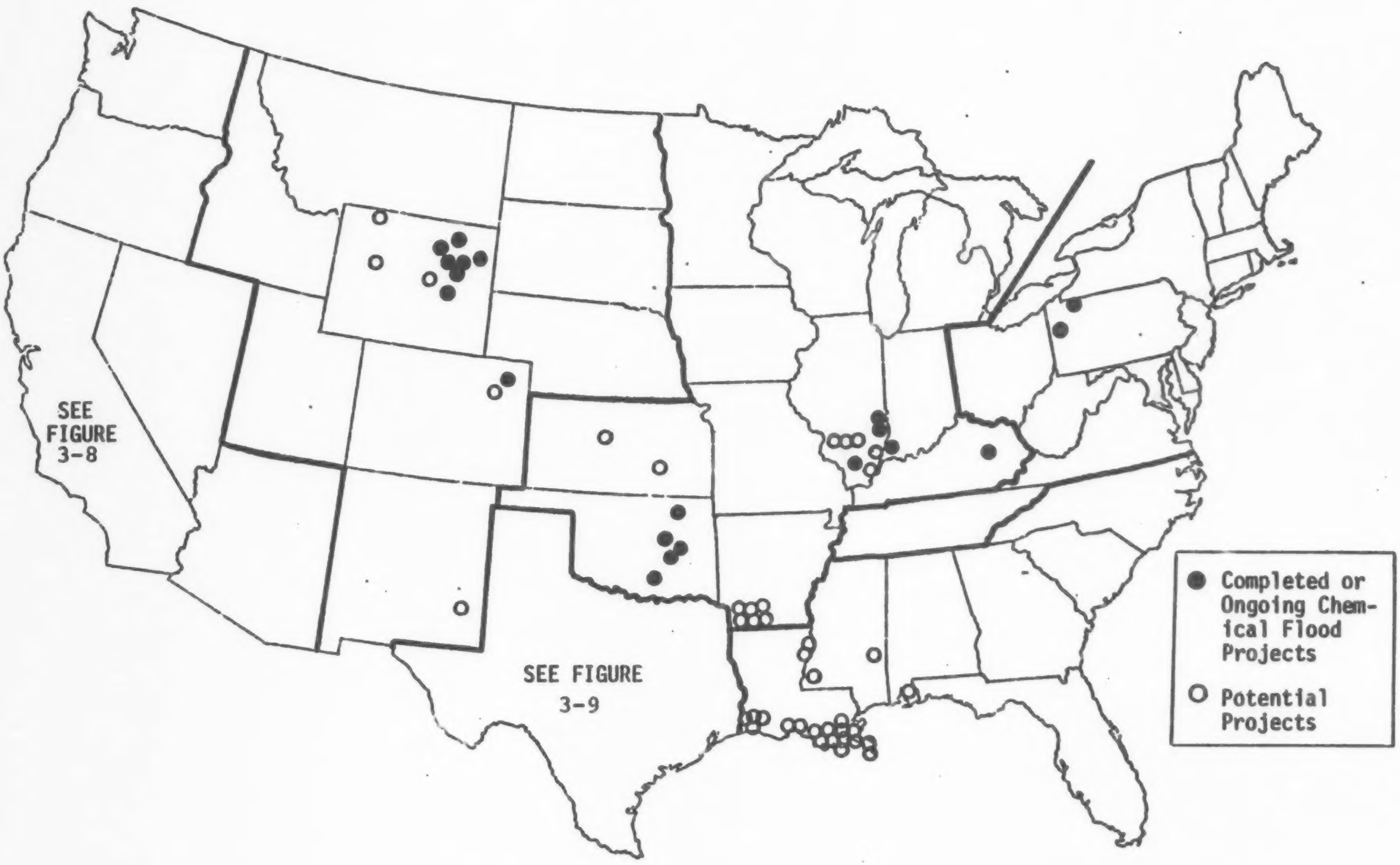

SEE FIGURE 3-8
SEE FIGURE 3-9
● Completed or Ongoing Chemical Flood Projects
○ Potential Projects

Figure 3-7. This figure illustrates the location of technically feasible micellar-polymer flooding projects in major oilfields.

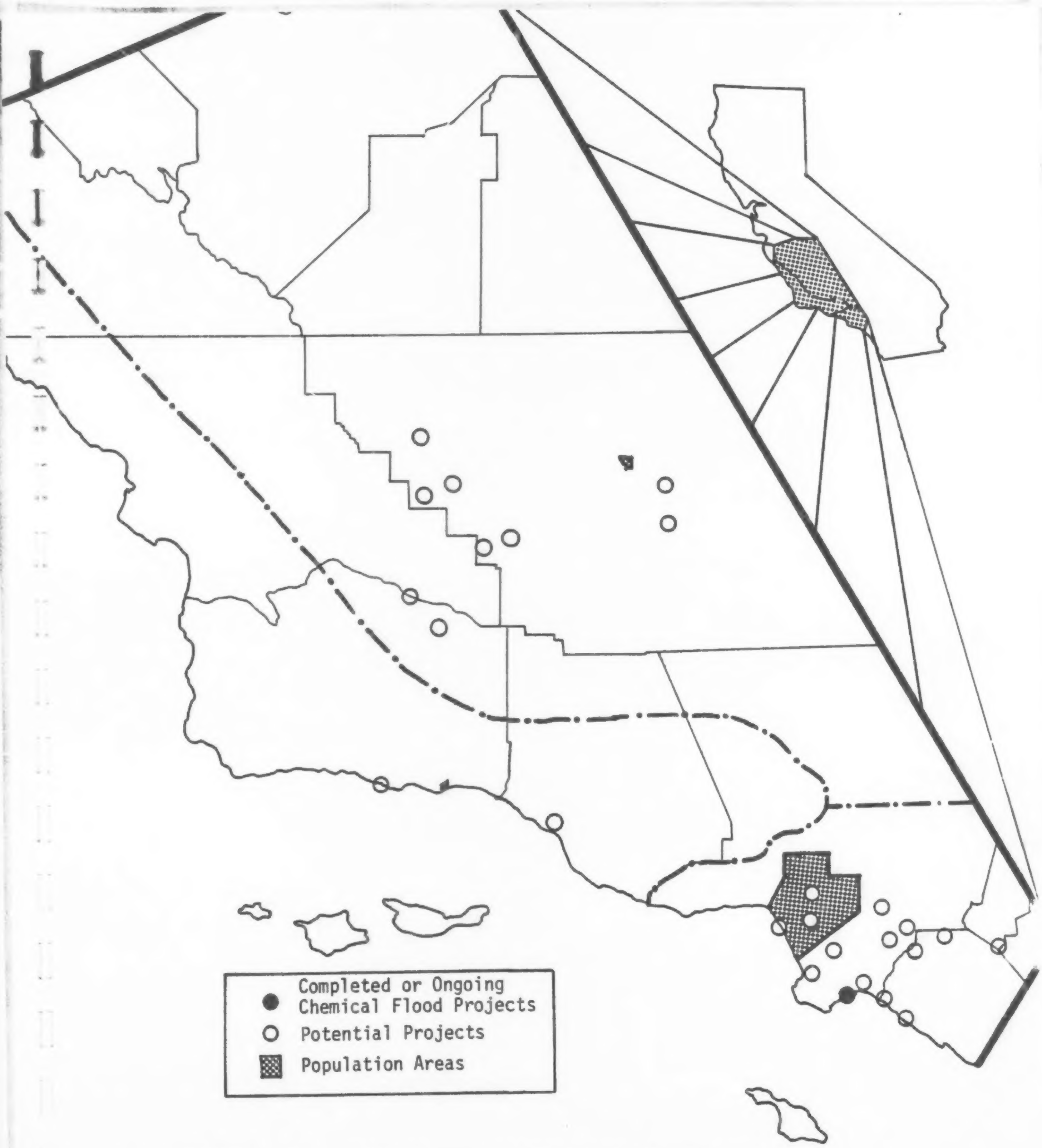

● Completed or Ongoing Chemical Flood Projects
○ Potential Projects
▨ Population Areas

Figure 3-8. This figure illustrates the location of technically feasible micellar-polymer flooding projects in major oilfields of Southern California.

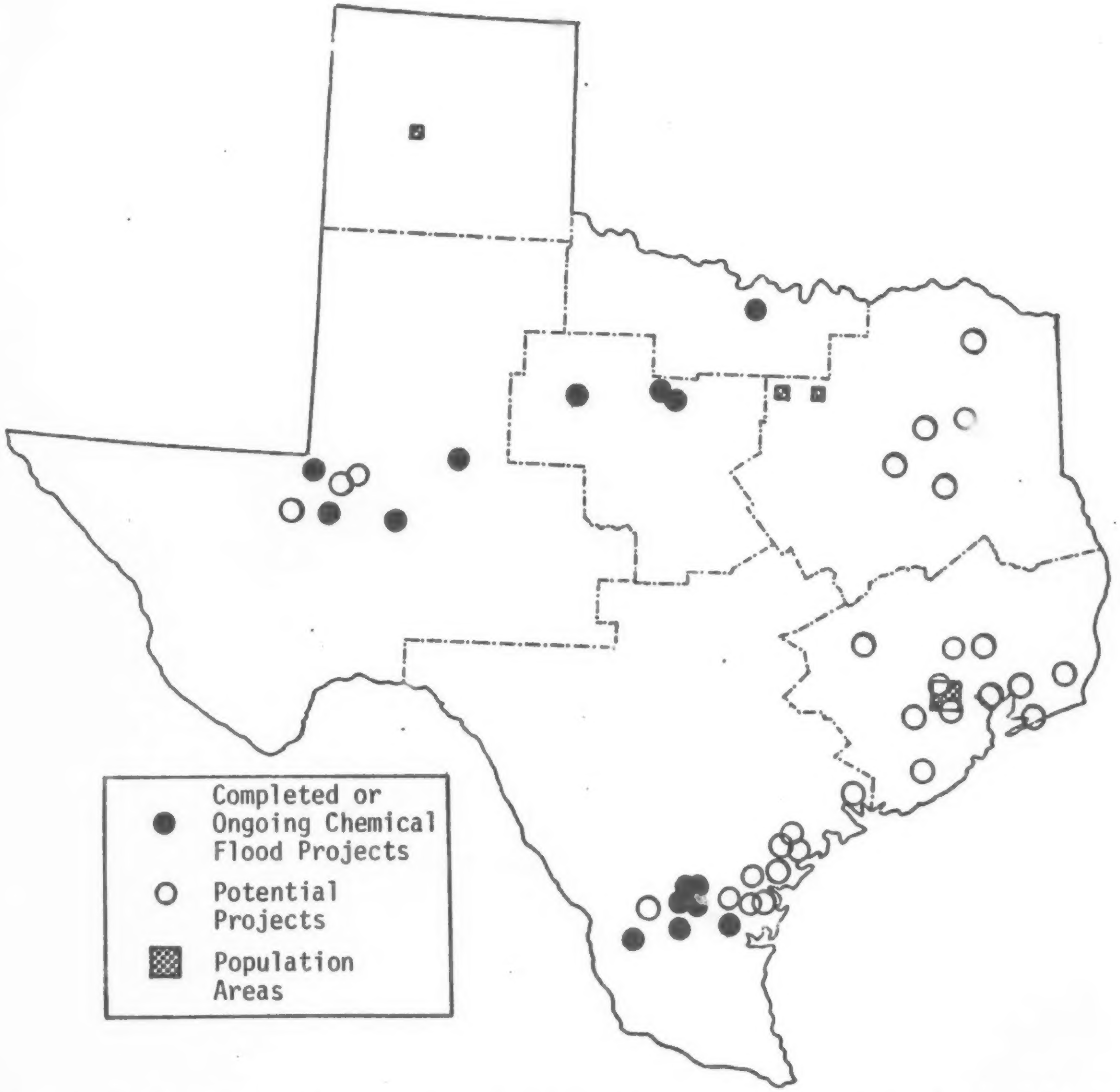

Completed or Ongoing Chemical Flood Projects
Potential Projects
Population Areas

Figure 3-9. This figure illustrates the location of technically feasible micellar-polymer flooding projects in major oilfields of Texas.

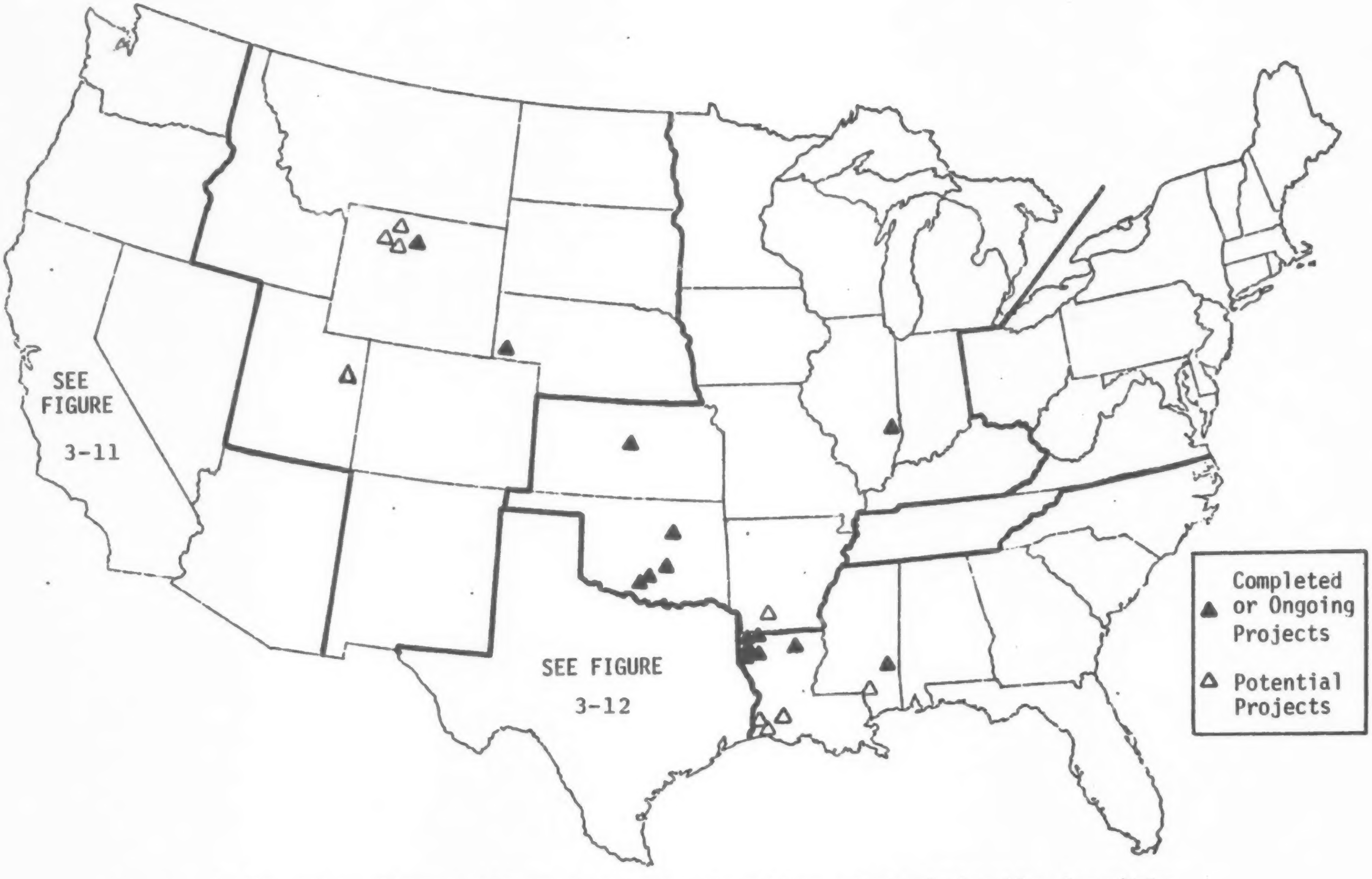
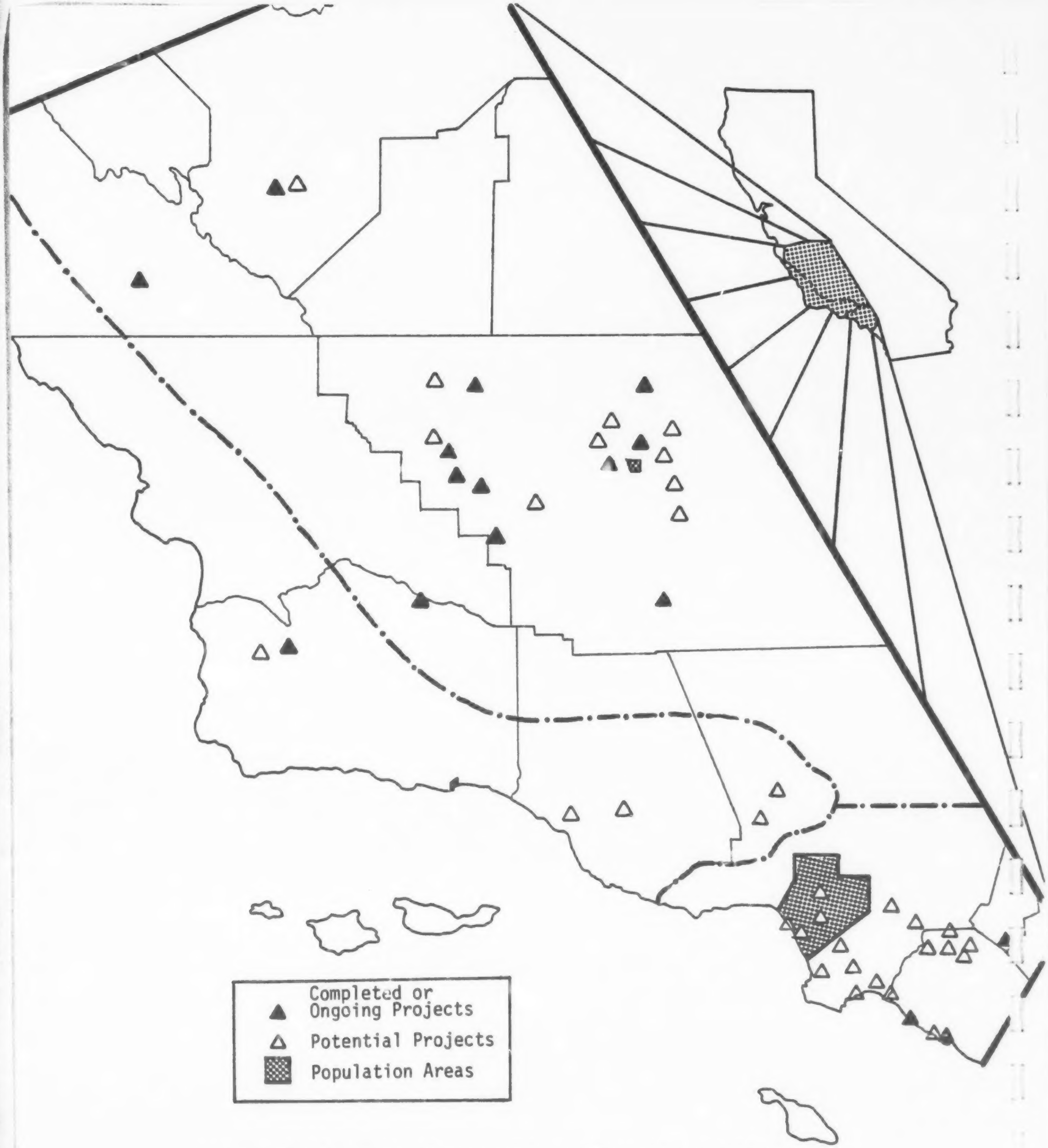

SEE FIGURE 3-11
SEE FIGURE 3-12
▲ Completed or Ongoing Projects
△ Potential Projects

Figure 3-10. This figure illustrates the location of technically feasible thermal tertiary recovery projects in major oilfields.



▲ Completed or Ongoing Projects
△ Potential Projects
▨ Population Areas

Figure 3-11. This figure illustrates the location of technically feasible thermal tertiary recovery projects in major oilfields of Southern California.

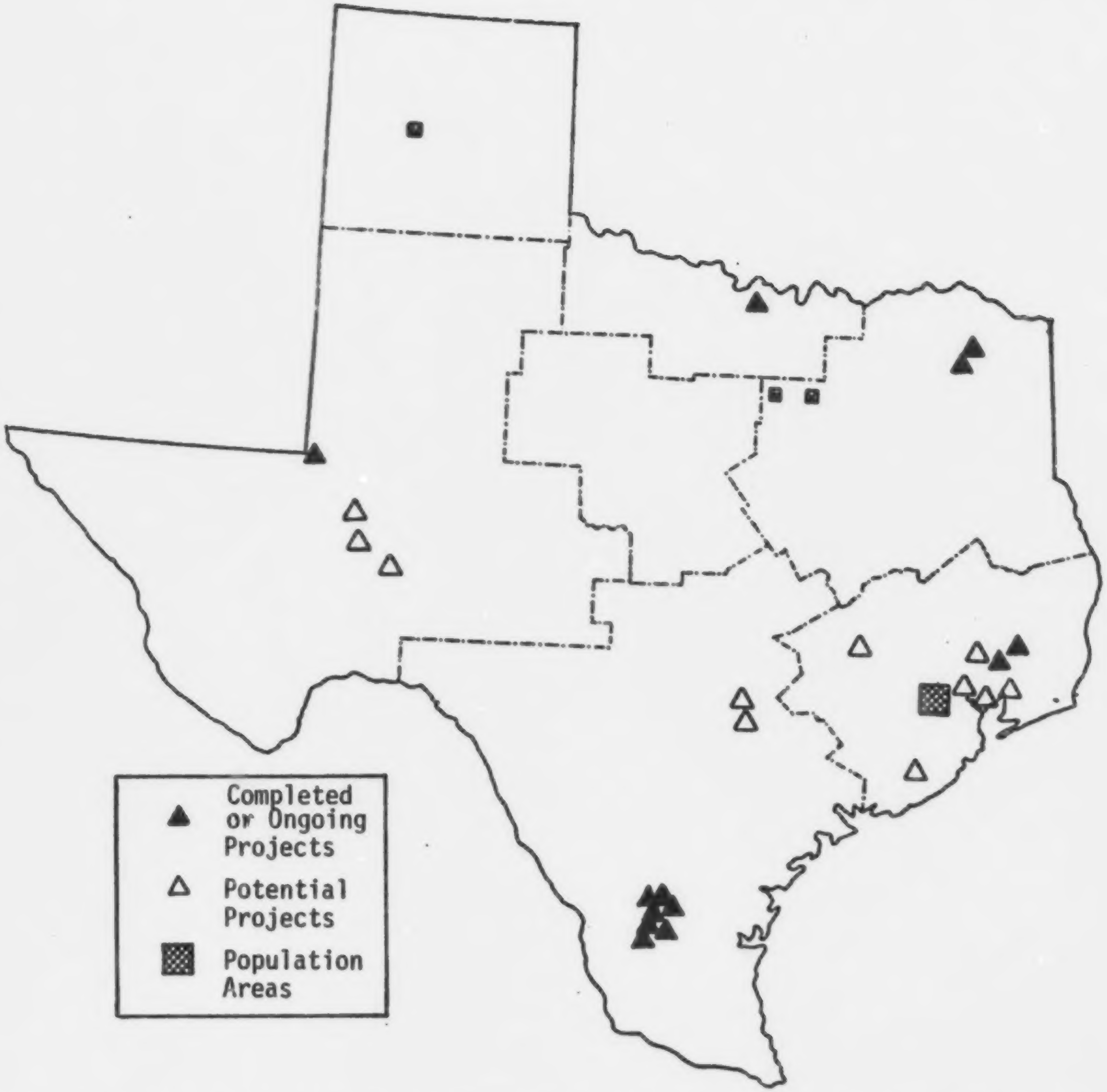

Completed or Ongoing Projects
Potential Projects
Population Areas

Figure 3-12. This figure illustrates the location of technically feasible thermal tertiary recovery projects in the major oilfields of Texas.

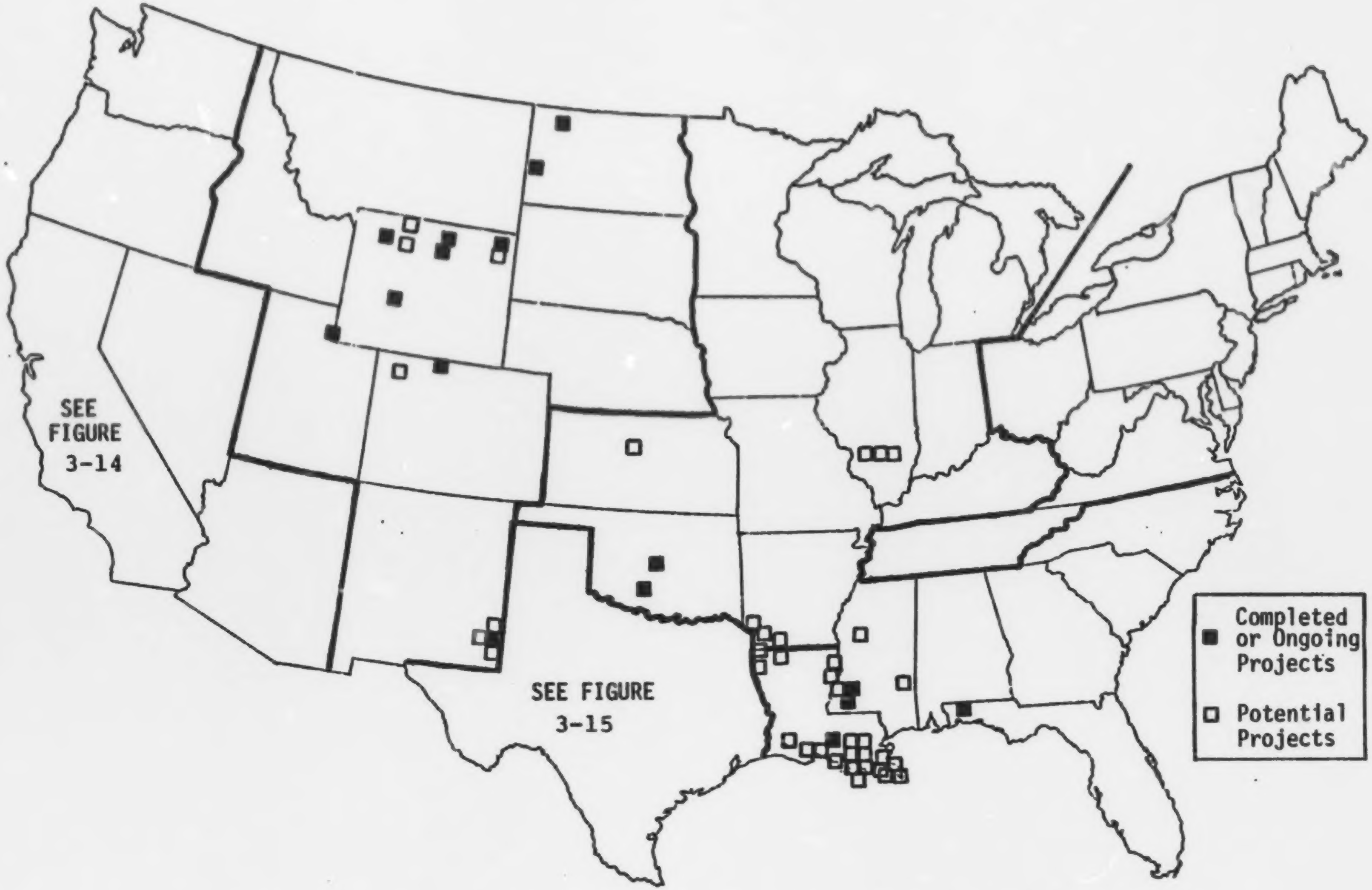

SEE FIGURE 3-14
SEE FIGURE 3-15
■ Completed or Ongoing Projects
□ Potential Projects

Figure 3-13. This figure illustrates the location of technically feasible miscible-CO_2 injection projects in major oilfields.

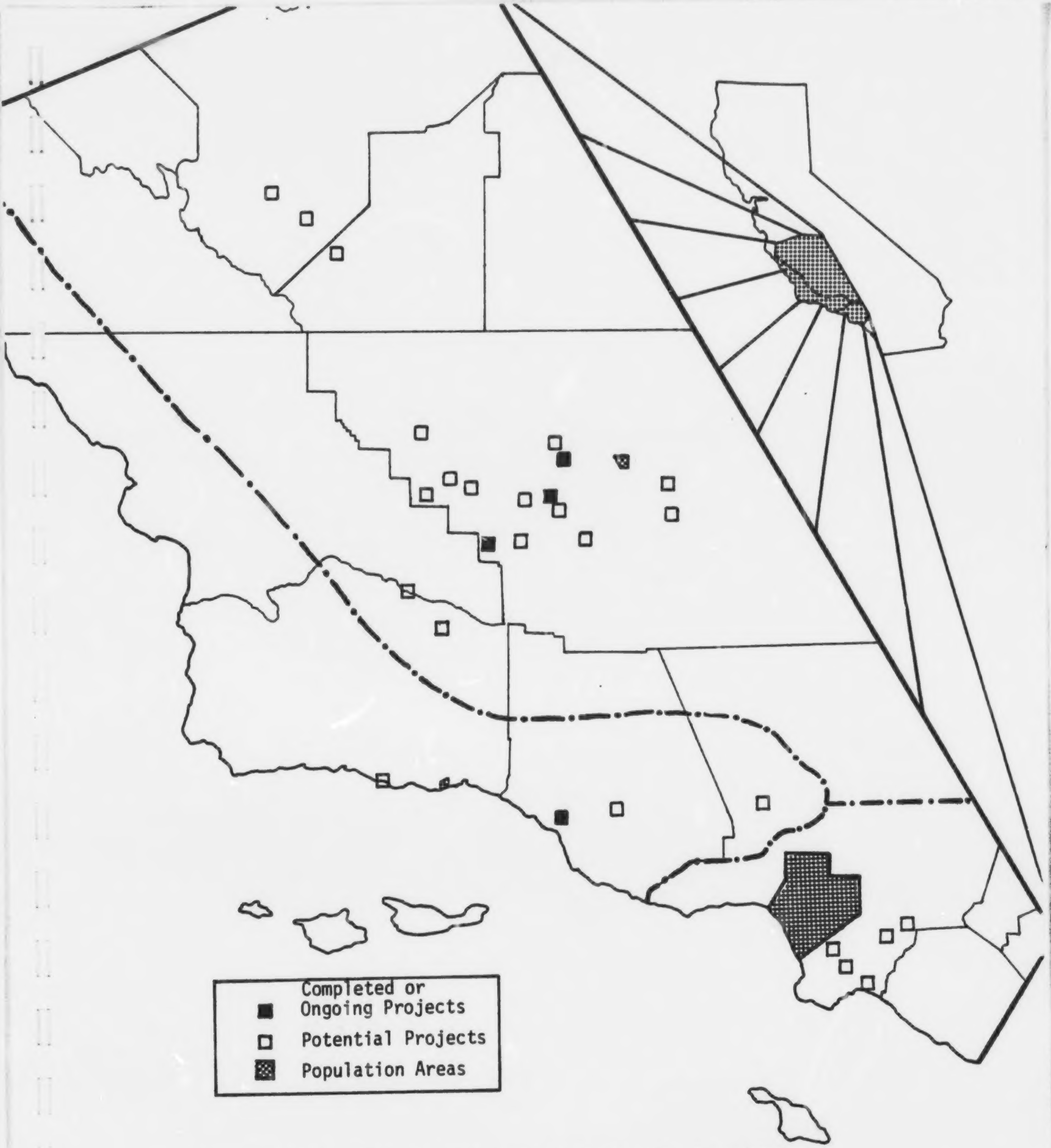

Completed or Ongoing Projects
Potential Projects
Population Areas

Figure 3-14. This figure illustrates the location of technically feasible miscible-CO_2 injection projects in major oilfields of Southern Calfornia.

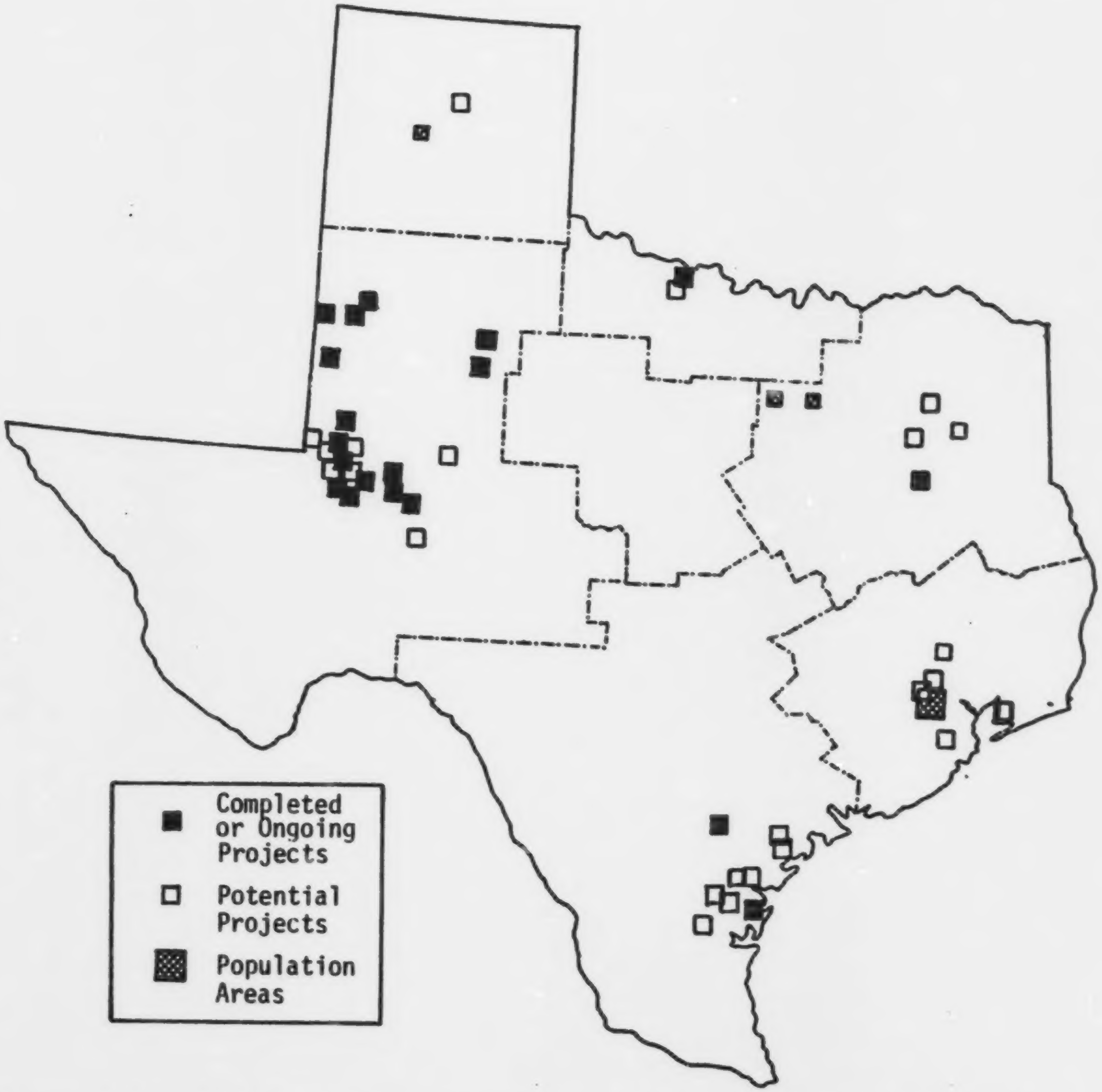

■ Completed or Ongoing Projects
□ Potential Projects
▨ Population Areas

Figure 3-15. This figure illustrates the location of technically feasible miscible-CO_2 injection projects in major oilfields of Texas.

sites where micellar-polymer flooding is technically feasible. The concentration of potential thermal recovery projects is greatest in the oil provinces of California in the Pacific West region as illustrated in Figure 3-10. The location of other oil fields where thermal methods appear to be technically feasible is shown in Figures 3-11 and 3-12. The fields where miscible carbon dioxide or gas recovery is feasible are identified in Figures 3-13 to 3-15. The South Central and Southeastern regions contain the largest concentration of potential projects using this technique.

The application of these tertiary recovery methods, where technically feasible in each region, will result in the forecasted 7 to 36 billion barrels of oil production. Regionally, the amount of oil produced by each method is unique. The estimated production of oil within each region by each method is presented in Table 3-7. The Pacific West region will obtain 89 to 96 percent of its tertiary oil production by thermal methods. It is estimated that as much as 4.7 billion barrels of oil will be obtained during the next 10 to 15 years. This production rate seems unlikely to be achieved and it appears that these first-order estimates have overstated the region's oil production during the period by a factor of four. With the exception of California, micellar-polymer flooding is likely to play a dominant role in tertiary oil recovery in each region as shown in Figure 3-16. The proportional production in each region by this method could exceed recovery by other methods by a factor of three and one-half to as much as ten times. The Rocky Mountain region shows a somewhat lower relative potential for this method because many of the fields included in analysis produce from reservoirs with low permeability/low porosity sandstones or carbonates and are highly fractured.

3.2.3 Limitations to Development

Though the potential production by tertiary oil recovery techniques is large and there are numerous locations where viable projects could be established, there are a number of factors limiting the rate of development to less than 36 billion barrels by 1990. During the transitional period, these limitations may include: transient excess demand for supplies of high quality water; shortages of chemicals, particularly surfactants and cosurfactants for micellar-polymer flooding; and state regulatory provisions. In each case, the extent of the limitation will be assessed and needs for change cited. The counteracting of surfactant shortages through on-site sulfonation of lease crude oil is a possibility which is also examined.

TABLE 3-7

TERTIARY OIL RECOVERY

ESTIMATED CUMULATIVE PRODUCTION FROM KNOWN OIL FIELDS IN THE UNITED STATES (EXCLUDING OFF-SHORE AND ALASKA)

(Millions of barrels)

REGION	RECOVERY TECHNIQUE USED			TOTAL PRODUCTION
	MICELLAR-POLYMER	THERMAL	MISCIBLE CO_2	
Pacific	10-500	1,870-4,700	70-100	1,950-5,300
Rockies	30-2,500	300-700	500-1,000	830-4,200
South Central (Texas)	80-6,600	500-1,200	800-1,500	1,380-9,300
North Central	60-5,000	800-2,000	300-500	1,160-7,500
Southeast	60-5,300	700-1,700	800-1,500	1,560-8,500
Northeast	10-1,200	80-200	30-100	120-1,500
TOTAL	250-21,100	4,250-10,500	2,500-4,700	7,000-36,300

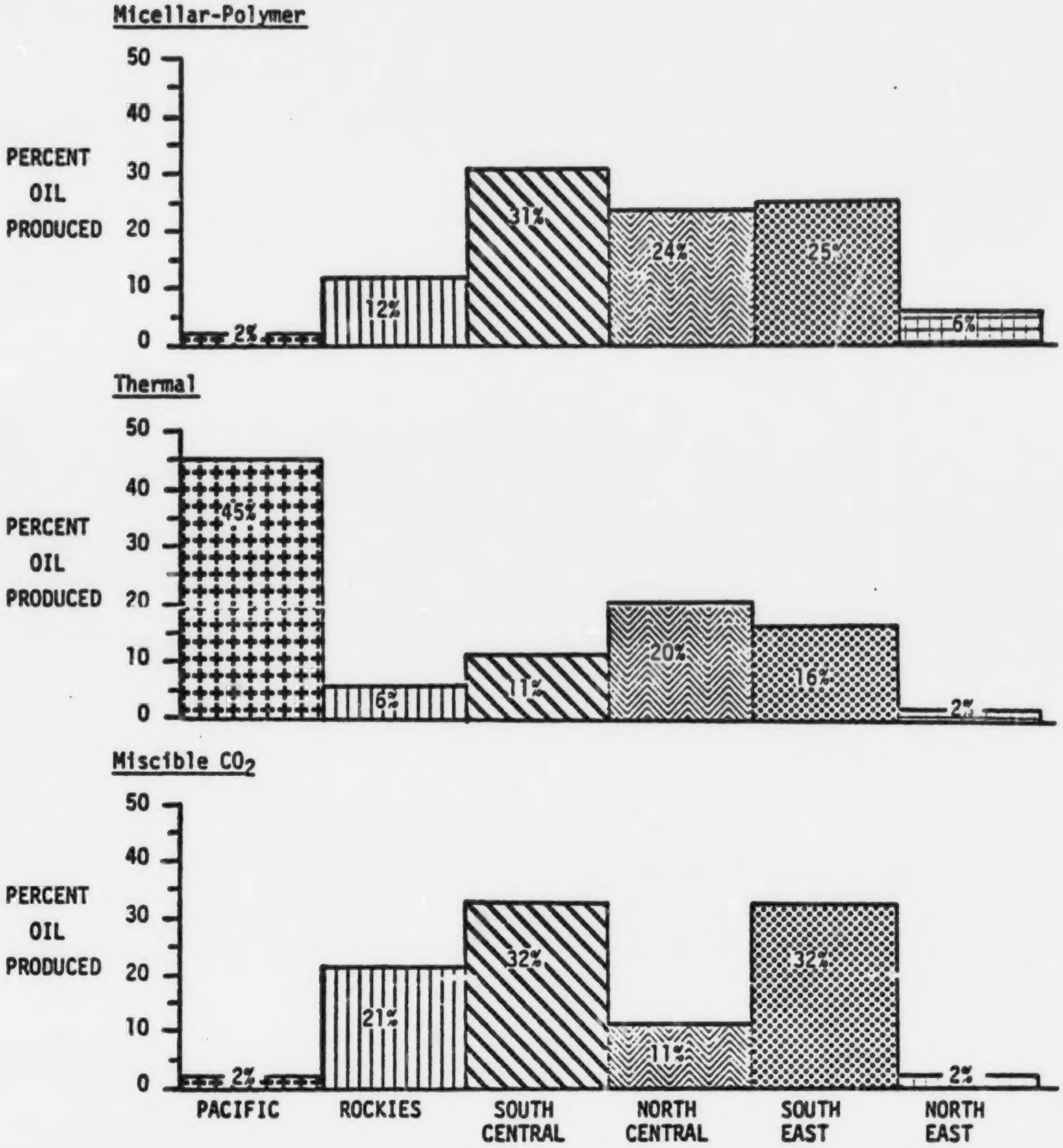


Figure 3-16. This figure is an illustration of the relative amount of oil expected to be produced by tertiary recovery methods in each region.

3.2.3.1 Chemicals

Given the potential oil recovery by tertiary methods of up to 36 billion barrels, the tertiary oil production rate has been estimated at 423 million barrels per year in 1985.[1] Micellar-polymer flooding techniques can be expected to contribute 200 to 250 million barrels to the forecasted total. The chemicals required to support this level of activity outstrip the current manufacturing capacity for polymers, surfactants and cosurfactants.

Table 3-8 shows the chemical availability situation for each of the materials currently in bulk use for oil recovery. Potential shortages could exist for each chemical and thereby limit the start of new recovery projects. Conversely, the demands will require newly-installed manufacturing capacity with resultant impacts of the discharges from these processes.

The supply of water-soluble polymers, which are used as thickening agents in the "mobility buffer" of a micellar-polymer flood, may fall short of demand by more than 100 million pounds by 1985. However, several factors should tend to mitigate this shortfall. The demand for polymers is expected to grow rapidly for other markets besides oil recovery -- most notable is the use of polymers as flocculants in wastewater treatment systems. Hence, the marketplace for polymers is broad-based so that manufacturers can build additional capacity without having to rely on a single type of customer or application to support the plants. Also, other potentially less expensive processes for producing polymers are available. The process of injecting a monomer into the oil-bearing formation under the proper conditions of pressure, temperature and catalysis to induce polymerization could be applied to mobility buffer solutions for tertiary recovery. Polymers have already been manufactured in this manner for other oil well treatment applications.[2] In addition to polyacrylamide, biopolymers such as polysaccharide can readily be manufactured from various media.

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[1] Gulf Universities Research Consortium, Planning Criteria Relative to a National RDT&E Program Directed to the Enhanced Recovery of Crude Oil and Natural Gas, Report No. 130, November 30, 1973.

[2] M.C. McLaughlin, "Method of Placement of Polymer Solutions in Primary Production and Secondary Recovery Wells," U.S. Patent 3,490,533 (January 1970).

TABLE 3-8

AVAILABILITY OF CHEMICALS FOR TERTIARY OIL RECOVERY

CHEMICAL	RAW MATERIALS	PROCESS	RECENT[a] PRICE $/lb	CURRENT SUPPLY 10^6 lb/yr	USAGE RATE lb/bbl OIL PRODUCED	ESTIMATED DEMAND 10^6 lb/yr	ESTIMATED DEMAND AS % CURR. SUPPLY	PHYSICAL FORM	COMMENTS ON AVAILABILITY
Polymers									
Polyacrylamide (partially hydrolized)	Acrylonitrile H_2SO_4	Hydration w/sulfuric neutralization, ion-exchange, polymerization and hydrolysis (partial)	1.50-2.00	50	1	210	> 400	Dry powder or liquid	Plant expansions likely to serve other growing markets (e.g. water treatment flocculants; Acryonitrile feedstock capacity 1,400 MM lbs/yr
Polysaccharide	Glucose xanthomonas campestris	Microbiological action	2.50/lb	40(2)			500	Powder	New plant capacity under construction should lead to significant price reduction
Surfactants									
Linear alkylbenzene sulfonates	Kerosene C_{10}-C_{13} or C_{11}-C_{14} SO_3, oleum NaOH	Separation of straight-chain paraffins, alkylation, sulfonation, neutralization	.10-.20 lb.	700-730	7-15	1470-3150	190-430	Viscous liquid	Possible production at oil refineries and on-site to meet needs
Alcohols									
Isopropanol	Refinery propylene H_2SO_4	Absorption in conc. H_2SO_4 hydrolysis of resulting isopropyl ester	.09/lb.	2,500	2-8	420-1780	16-67	Anhydrous liquid	Common alcohol, short-term shortages possible. Least expensive cosurfactant
Pentanol	Pentene	Hydration and acid	.18/lb.	NA			NA	Liquid/low viscosity	
Hexanol	Hexene	Hydration and acid	.24/lb.	NA			NA	Liquid/low viscosity	
n-Butanol	(1)croton-aldehyde from ethyl alcohol (2)Propylene, CO, H_2	Reduction by catalytic hydrogeneration Oxo process - propylene to n-butyraldehyde, isobutyaldehyde	.16/lb.	660			65-250	Liquid	Possible use as substitute during shortages
iso-Butanol	Propylene CO, H_2	Oxo process (as above)	.16/lb.	170			250-1,000	Liquid	

[a] FOB Plant

The polysaccharide for tertiary oil recovery which is manufactured by a division of Kelco Chemical Company is produced by the microbial action of a strain of bacteria on glucose. The high cost of polysaccharide indicated in Table 3-8 reflects the high prices for sugar and corn during recent shortages. However, use of process materials other than glucose is feasible which could reduce the cost of polysaccharides. Municipal sewage sludge could serve as a medium for the production of polysaccharides for tertiary oil recovery applications. Though yields of polymer from sludge are expected to be low, its low cost and large, stable supply make sludge an attractive new medium for producing the needed quantities of polymer.

Surfactants will show a shortfall of 600 to 2,500 million pounds by 1985 based on current capacity. Major refiners and specialty chemical manufacturers have stated that they will build the plant capacity needed to serve this demand as soon as it materializes. Certainly, supply and demand will come into closer balance in the long term. However, large shortages may still exist during the transitional period due to the time lags in the construction of new chemical facilities. For tertiary oil production to achieve forecasted levels during the 1985-1990 time frame, alternative sources of sulfonates will be required. An important factor for petroleum sulfonates is transportation cost. Petroleum sulfonates are highly viscous liquids which must be transported in steam heated tankers to facilitate loading. This fact discourages long distance multi-mode movement of large quantities of surfactants. Trucking charges are estimated at 3 to 4 cents per pound per 100 miles. Therefore imports of sulfonates are likely to be limited. Yet, the typical micellar-polymer project in a field with 5 million barrels of oil remaining in place would require approximately 500 tanker truckloads of surfactants over a few months of time while the slug was being prepared and injected.

To fulfill immediate needs, sulfonation units must be built. The process of sulfonation is basically simple and straightforward and achieves yields of 10 to 15 percent per treatment in large scale operations. The simplicity of the process and the high cost and logistical difficulties of transporting the end-product give the integrated petroleum company a number of options for providing its own petroleum sulfonates. As an operator of micellar-polymer flooding projects, the company may choose the location for the sulfonate plant and feedstock inputs. These choices are illustrated in Table 3-9. The Option I to produce sulfonates at a refinery will be chosen by operators whose project oil fields are nearby their refineries and where the capacity is

TABLE 3-9

TERTIARY OIL RECOVERY

OPTIONS IN MANUFACTURING SULFONATES

		PLANT LOCATION	
		At Refinery	In the Field
FEEDSTOCK	Lubricating Stocks	I High transportation cost High yield (Up to 15% per pass)	II Low to High transportation cost Moderate yield (Up to 8% per pass)
	Crude Oil	III High transportation cost NOT PRACTICAL Low yield	IV Low transportation cost Low yield (5% per pass)

added to serve commercial as well as "captive" demand and where the unsulfonated crude fraction would be incompatible with the slug. Figure 3-17 indicates the location of existing refineries where sulfonation units might be constructed. Marathon has chosen this approach in Illinois where its oil field is adjacent to the refinery. However, refinery operating plans may not be geared to manage such a unit or may already use the lubricant stock in another part of the process. Option II may be chosen to overcome the possible conflicts between field and refinery operations. The sulfonation unit would be built on-site at the oil field and would be sized to local requirements for sulfonates. If available, lubricating stocks could be transported to this facility from the refinery although savings in transportation costs are sacrificed. The appeal of this option and option IV is that on-site manufacturing may reduce transportation costs and provide sulfonates for planned projects quickly and independently of commercial chemical markets. Either a lubricating stock refined on-site from crude oil or the crude oil itself could be used as a feedstock. Not all oils may prove to be suitably reactive for economic sulfonation, or compatible with the microemulsion slug, but as indicated on Table 3-10 the costs of sulfonating lease crude on-site might compete with market prices. Further study and analysis is required to determine the feasibility of field sulfonation and its impact on the environment as micellar-polymer projects are established.

Cosurfactants are not as severe a constraint to the development of micellar-polymer flooding. Though propanol is preferred due to its low cost, there are alternative alcohols available which might serve as substitutes. These include pentanol, hexanol, butanol, phenol, and cresol. Since sufficient supplies of a particular cosurfactant are required to fulfill the entire "recipe" for the micellar slug at a given project, regional variations in the availability and use of various cosurfactants could develop.

3.2.3.2 Water Supplies

The availability of suitable water for preflushing preparation of the micellar slug and the mobility buffer and follow-up injection is important to the success of a tertiary oil recovery project. Water with low concentrations of divalent ions and total dissolved solids is required. Connate water in the reservoirs is rarely suitable for reinjection without treatment to remove high concentrations of divalent ions. Concentrations (milligrams per liter) of

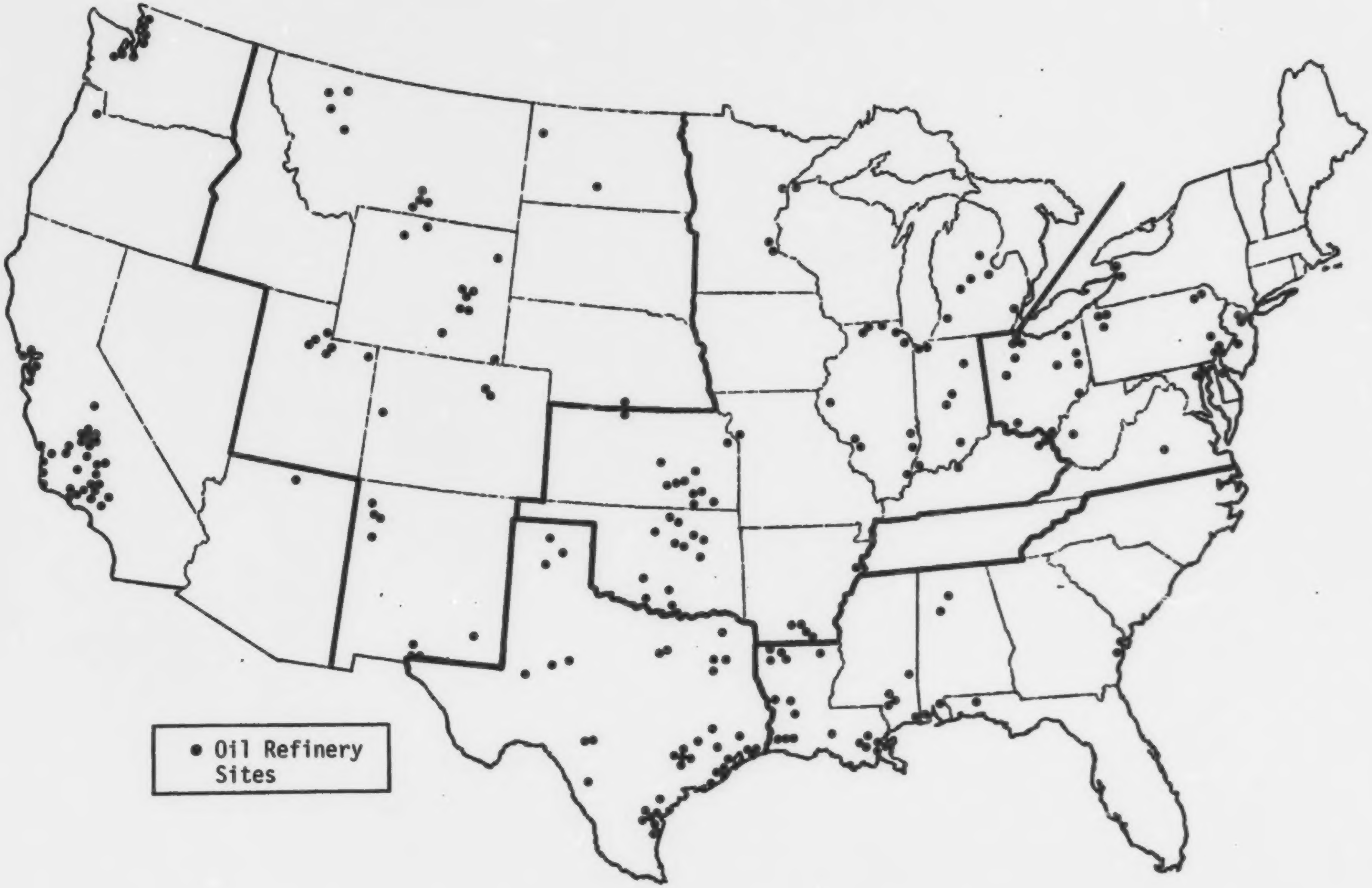
● Oil Refinery Sites

Figure 3-17. This figure illustrates sites of existing oil refineries where new sulfonation units could be constructed to serve tertiary oil projects.

TABLE 3-10

TERTIARY OIL RECOVERY

OILFIELD MANUFACTURE OF SULFONATES

(Cents per pound of Sulfonate)

	COMMERCIAL MARKET PRICE (DOLLARS)	ON-SITE COST (DOLLARS)
Petroleum Sulfonates (Mahogany acid)	0.20	0.03[a]
Raw Materials:		
Sulfur Trioxide		0.10
Isopropanol	0.04	0.04[b]
Sodium Alkaline Salts		0.05
Utilities	0.01	0.02
Transportation (250 mi)	0.10	0.03
Fixed Costs per lb.[c]		
25 MM lb/yr		0.05
150 MM lb/yr		0.02
Cost per lb.	0.35	0.29 - 0.34

[a] "Opportunity Cost" -- One pound of oil at $11 per barrel.

[b] Alcohol is used in this process and is available for use as a cosurfactant thus cost included.

[c] Two-year amortization, includes operating costs.

calcium and magnesium, respectively, in connate waters average 2,530 and 530 in tertiary formations, 25,800 and 2,500 in Pennsylvania formations.[1] These concentrations are 5 to 50 times the acceptable levels for successful micellar flooding.

Supplies of suitable water for a large-scale micellar-polymer flood may not be available. At present, some strains on water resources have occurred with pilot scale projects. The Cities Service/Energy Research and Development Administration project near El Dorado, Kansas, has built a five-mile long water pipeline six inches in diameter from the town's lake (raw water supply) to the oil field. The design water flow rate for the pilot-scale project is 6,300 barrels per day (264,600 gallons per day).[2] This represents approximately 20 percent of the estimated daily water consumption by El Dorado's 13,000 residents. Since there are more than 6,200 acres of Admire sand in the El Dorado field while the tests cover only 51.2 acres, there is a potential demand at the field for as much as 800,000 to 1,500,000 gallons per day of high quality water from the town's supply, assuming a development rate of 300 to 600 acres per year and a well density one-half as great as the pilot test area.[3]

Surface waters such as rivers may be unacceptably high in TDS and divalent ions as are shallow unconsolidated aquifers which are subject to evaporative concentration of salts. The difficulty of further defining the effect of water supply availability is the need for detailed data on local consumption trends, availability of undeveloped, uncommitted water resources and the scale and timing of the development of micellar-polymer oil recovery projects. These local shortages of suitable water might lead to on-site water treatment and recycling as part of the project plan, a factor which would tend to reduce the amount of oil economically recoverable by micellar-polymer flooding if not making the project economically unattractive.

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[1] A.G. Collins, "Chemical Applications in Oil and Gas Well Drilling and Completion Operations." (unpublished)

[2] Cities Service Oil Company, El Dorado Micellar-Polymer Demonstration, BERC/TPR-75/1, October 1975.

[3] If the field were controlled by a number of operators who undertook simultaneous fieldwide development projects, water usage would be 20 to 25 million gallons per day.

3.2.3.3 Current Regulations

The amount of oil recovered through tertiary operations depends upon technology and prices. These factors, however, do not operate freely; governmental regulation of petroleum production is far-reaching, indeed. Every major oil producing state controls to some extent the operations of the petroleum industry within its borders. Although the various state codes are not uniform, most do have certain features in common. In particular, they are characterized by rules governing fluid injection, well spacing, allowables, unitization and plugging. A brief analysis of this partial list will indicate the possible impacts on tertiary recovery projects of current industry regulations.

Fluid injection rules perhaps most clearly affect tertiary recovery. Their impact, however, does not appear to be great. Designed primarily to protect subterranean freshwater supplies and oil reservoirs beneath adjacent land tracts, these regulations generally require administrative approval of all injection operations. Unless objections are raised, however, permission is usually granted. The Illinois rule is typical. Basically, it demands notice to all adjacent well owners within a half mile radius, specifies a 10-day objection period, and requires a hearing if complaints are lodged.

Traditional well spacing requirements are less neutral. Designed to prevent excessively rapid depletion of all reservoirs during primary recovery, they may prove too strict for tertiary operations. Not only do tertiary projects need nearby injection wells, but they sometimes also require the clustering of production wells for maximum coverage and efficiency. North Dakota's code -- specifying that wells in the same pool be located at least 1,000 feet from each other and 500 feet from the nearest property line -- is not entirely atypical. Certainly, it does not appear tailored for tertiary recovery projects. With this spacing, a typical micellar-polymer flood could require more than eight years to complete -- a time frame which adversely affects the economics of the project.

Although spacing requirements frequently may be waived on a case-by-case basis after commission hearings, a more reasonable approach may be to establish separate guidelines for tertiary projects. Illinois even goes to the length of exempting fluid injection programs from spacing requirements altogether.

Unlike spacing rules, allowables do not directly prevent the drilling of new wells; however, indirectly they may inhibit the drilling operations required for successful tertiary recovery. Essentially, an allowable is the production limit -- set by the regulatory agency -- of a particular well in a particular field. If the establishment of an allowable for a new tertiary production well means that allowables for old wells in the field must drop -- to maintain the same total field allowable -- then there is little incentive for an overall field owner to undertake tertiary recovery. Yet, simply eliminating total field allowables is not necessarily the answer. However, a sound overall conservation policy which takes into account conventional as well as tertiary recovery operations may demand it. More than this, an operator is not induced to change a marginal producing well to an injection well if he will lose the allowable of the converted well without gaining on other wells. Texas does provide for allowable transfers; this practice should be considered elsewhere. Maximum Efficient Recovery (MER) rates are the basis for these regulations, but a great deal of additional research is needed to redefine MERs in view of the latest technologies.

Allowables may be a problem for tertiary operations even if their impact on the overall field is ignored. At this early stage of development, tertiary recovery is a risky venture. The return associated with that risk can be increased by raising or eliminating allowables on wells in a tertiary recovery project. Interest rates make a dollar today worth more than a dollar a year from now. Since oil is money, the companies that produce it want to finish their operations as quickly and efficiently as possible. Insofar as allowables restrict production, they defer the payoff and hence inhibit tertiary recovery. Some states' allowables on tertiary projects are higher than their allowables on primary wells of the same depth, but the bonus may be insufficient in light of the risks associated with tertiary projects.

Not only do allowables restrict the rate of cash flow from tertiary operations; they may also restrict the ultimate amount of cash flow. The recovery processes employed are most effective during relatively short peak times. This implies a corresponding high level of recovery. Restriction placed on production by allowables will in these cases unreasonably extend the recovery period, thus reducing the efficiency of recovery and perhaps reducing the total amount of recovery as well. A regulation established presumably to conserve oil during primary stages may waste it during tertiary stages if a so-called tertiary recovery method is deferred past the time of its most profitable application.

Oil conservation perhaps most clearly emerges in the issue of unitization. Field unitization means cooperative development by all producers to maximize recovery. Since fluids injected into one area of a field may migrate unpredictably through strata to affect production in an area controlled by other interests, the need for common development is of particular importance. Most states require full unitization if two-thirds to three-quarters of the royalty owners and operators agree. However, few if any place oil conservation on a higher plane than property rights and demand commonality with less than substantial majority consent. Texas has no involuntary unitization law at all. Lack of unitization may also eliminate many smaller fields from every undergoing tertiary recovery. This problem could limit advanced recovery in areas such as the Denver-Julesberg Basin with many scattered small pools, and in states such as Illinois where oil production properties have passed through several generations of ownership.

Concern for water conservation has led to the almost universal adoption of plugging regulations by the states. Though perhaps effective for this purpose, these provisions reduce the profitability of tertiary recovery by raising the costs of reentering old wells. For most areas these costs are prohibitive. Plugging regulations generally leave the design in the hands of the operator with approval by commission inspectors.

The current regulatory framework surrounding the petroleum production industry appears designed largely for problems associated with primary and secondary operations. The emergence of a new recovery technology has created a new set of problems, which in turn may require new regulations. At the very least, the present codes need to be reconsidered; very likely, they will require revision, as well.

CHAPTER FOUR

HAZARDS OF TERTIARY OIL RECOVERY

4.0 Introduction

There are several possible sources of environmental hazards stemming from tertiary oil recovery. Chemicals used in micellar-polymer floods represent the most clearly identifiable group of potential hazards. These are of special concern because many will be left behind in the reservoirs after the recovery project is completed. The primary reservoir remnants of carbon dioxide and thermal methods are low pH brines. The composition of produced gases from fireflooding and steam injection is not well-understood, but some initial estimates of the movement of sulfur dioxide and oxides of nitrogen have been made. Fugitive emissions of hydrocarbon vapors from these sources needs further study. Gaseous streams from production wells in thermal recovery projects and emissions from steam generator stacks are two sources of potential airborne hazards introduced by tertiary oil recovery. The sources of these potential hazards from each recovery method are analyzed and the toxicity and/or carcinogenicity of the materials are presented.

4.1 Chemical Hazards

Tertiary oil recovery processes employ a variety of chemicals. In micellar-polymer flooding, chemicals such as surfactants, polymers and cosurfactants are used. Tables 4-1 through 4-6 list some of the compounds in each class which are in use or have been proposed for use in U.S. patents and the literature. Tables 4-7a and 4-7b list chemicals used on infrequent occasions in connection with thermal recovery processes. The choice of chemicals depends upon: (1) availability of the chemicals, (2) costs of the chemicals, (2) chemical compatibility with the specific reservoir characteristics encountered, and (4) the required concentrations of the chosen chemicals in the reservoir to achieve additional oil recovery.

If in the recovery process chemicals escape to the environment in sufficient quantities, their presence can degrade water supply quality and destroy biota. The release of chemicals may occur at the manufacturing plant, on the

TABLE 4-1

TERTIARY OIL RECOVERY

CHEMICALS PROPOSED FOR USE AS SURFACTANTS

Ditetradecyl dimethyl ammonium chloride
Dodecyl trimethyl ammonium chloride
Hexadecyl trimethyl ammonium chloride
Alkyl phenoxypolyethoxy ethanol
p-Chloroaniline sulfate laurate[1]
p-Toluidene sulfate laurate
Polyglycerol monolaurate
Glycerol disulfoacetate monomyristate
n-Methyltaurine oleamide
Monobutylphenyl phenol sodium sulfate
Polyoxyethelene alkyl phenol
Morpholine stearate
Pentaerythritol monostearate
Dihexyl sodium succinate
Diethyleneglycol sulfate
Sodium sulfate oleylethydanilide
Alfa olefin sulfonate
Alkyl aryl sulfonate
Alkyl aryl napthenic sulfonate with monovalent cation
Hexadecylnapthalene sulfonate
Sodium lauryl sulfonate
Triethanolamine laurate
Triethanolamine myristate
Triethanolamine oleate
n-Dodecyl-diethleneglycol sulfate
Sodium glyceryl monolaurate sulfate

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[1] Halogenated compounds, though proposed in the literature, are unlikely to be used in field operations because their possible presence in produced oil streams would poison the catalysts at the refinery.

TABLE 4-2

TERTIARY OIL RECOVERY

MATERIALS PROPOSED FOR USE AS MOBILITY BUFFERS

Aldoses
  B series
  L series
Amines
Carboxymethylcellulose
Carboxyvinyl polymer
Dextrans
Desoxyribonucleic acid
Glycerin
Ketoses
  B series
  L series
Polyacrylamide*
Polyethylene oxide*
Polyisobutylene in benzene
Rubber in benzene
Saccharides
  Conjugated saccharides
  Disaccharides
  Monosaccharides
  Polysaccharides*
Tetrasaccharides

*Most commonly used

TABLE 4-3

TERTIARY OIL RECOVERY

HYDROCARBONS USED AS FRACTION OF MICELLAR SLUG

(Or in Miscible Displacement Processes)

Alkylated aryl compounds

Anthenic compounds

Aryl compounds with mono cyclic compounds
  Alkyl phenols
  Benzene
  Toluene

Aryl compounds with polycyclic compounds

Crude oil*

Partially refined fractions of crude oil
  Overheads from crude columns
  Side cuts from crude columns
  Gas oils
  Straight run gasoline
  Kerosene
  Liquified petroleum gas
  Napthas
  Heavy napthas

Refined fraction of crude oil
  Paraffinic compounds
    Decane
    Dodecane
    Heptane
    Octane
    Pentane
    Propane
    Cycloparrafinic compounds
    Cyclohexane
Napthenic compounds

*Most commonly used

TABLE 4-4

TERTIARY OIL RECOVERY

CHEMICALS PROPOSED FOR USE AS ELECTROLYTES

- Acids
    - Hydrochloric acid
    - Inorganic acids
    - Organic acids
    - Sulfuric acid
- Bases
    - Inorganic bases
    - Organic bases
    - Sodium hydroxide
- Salts
    - Inorganic salts
    - Organic slats
- Sodium hydroxide
- Sodium nitrate
- Sodium sulfate

TABLE 4-5

TERTIARY OIL RECOVERY

CHEMICALS PROPOSED FOR USE TO BLOCK EXCHANGE SITES IN THE FORMATION

(Preflushing)

Quarternary ammonium salts

Fluoride solutions

Potassium permanganate

Sodium hydroxide

TABLE 4-6

TERTIARY OIL RECOVERY

CHEMICALS PROPOSED FOR USE AS COSURFACTANTS

- Alcoholic liquors
  - Fusel oil
- Alcohols
  - Alkaryl alcohols
    - Phenol
    - p-Nonyl phenol
- Amyl alcohols
  - Isopentanol*
  - 2-pentanol*
- Cresol
- Decyl alcohols
- Ethanol
- Isobutanol
- n-Butanol
- Cyclohexanol
- 1-Hexanol*
- 2-Hexanol*
- 1-Octanol
- 2-Octanol
- Isopropanol*
- Aldehydes
  - Formaldehyde
  - Gluteraldehyde
  - Paraformaldehyde
- Amides
- Amino compounds
- Esters
  - Sorbitan fatty ester
- Ketones

*Most commonly used

TABLE 4-7a

TERTIARY OIL RECOVERY

CHEMICALS PROPOSED FOR USE TO INITIATE IGNITION OF IN-SITU COMBUSTION

Hydrazine

Hydrogen peroxide

TABLE 4-7b

TERTIARY OIL RECOVERY

CHEMICALS PROPOSED FOR USE TO INCREASE EFFICIENCY OF THERMAL METHODS

Quinoline

Sodium hydroxide

Toluene

transportation route, at the oilfield site during preparation of the chemical for use, from the reservoir (during the actual tertiary recovery process), and from the reservoir (after completion of the tertiary recovery process). Many of these activities are within the scope of existing EPA regulations. The potential environmental hazards associated with the handling of these chemicals on the surface are clearly identifiable. However, the presence of concentrations of chemicals in the oil-bearing formations represents a long-term source of pollutants that may be released underground into nearby aquifers at some unknown time in the future. Therefore, an understanding of the potential hazards of chemicals at reservoir conditions is important.

Chemicals which reach the environment may affect it in a number of ways. Living organisms exercise natural quality controls, both on freshwater and seawater. Some chemicals or their degradation products may eliminate those beneficial organisms in certain areas, or they may decimate only certain species or certain developmental stages. For example, the adult organism may migrate into an area where reproduction is inhibited. The food sources for these organisms may be more sensitive to certain toxic materials than the organisms themselves are; and the beneficial organism populations may become reduced because of a lack of food, rather than by a direct toxic effect upon the organisms.

All of the general types of toxic effects mentioned above and the specific effects to be mentioned later are concentration dependent. Chemicals which may be released from an oil reservoir decrease in concentration because of dilution, filtration, adsorption on both soil and clay particles, precipitation, chemical decomposition or polymerization, and biodegradation with time and distance travelled through an aquifer. The effects of a chemical used in tertiary oil recovery may well be negligible at the levels actually encountered in the vicinity of the recovery site. Furthermore, there is only a possibility that it will ever reach a water body as discussed in Chapter Five. Nevertheless, most of the chemicals used in tertiary oil recovery have definite and well-documented effects on water quality, and many others have documented toxic or carcinogenic effects on animals. It is recognized that the synergistic effects of certain combinations of pollutants portend greater or lesser risks than the simple additive combination of the effects of each pollutant. However, synergistic toxicity studies of chemicals used in micellar-polymer flooding are not available in most instances and such work is not within the scope of this investigation.

Another important aspect of toxicity is the composition of the ecosystems which are contacted by the pollutants. Definition of these ecosystems and analysis of chemical toxicity data for each ecosystem including questions of biodegradation and bioconcentration are also of concern, but have not been undertaken in this study.

The surfactants listed on Table 4-1 have been considered for use in micellar slugs. The ones most commonly used are long-chain, linear alkyl sulfonates such as lauryl sulfonate and duodecyl sulfonate, and alkyl aryl sulfonates. These substances are also used as foaming agents and detergents, and their most noticeable water quality effect, at least in high concentrations, is to produce rather ugly foams, both in water bodies and at the tap (if sulfonate-containing water is used as a source of a public water supply). The linear alkyl sulfonates are biodegradable at fairly rapid rates. Surfactants, or surface-active agents, also may impart tastes or odors to water as indicated in Table 4-8.

Toxic effects to aquatic life have been reported for alkyl sulfonates at concentrations which are exceeded in reservoir fluids during micellar-polymer flooding. Reservoir concentrations may be 375 to 1,900 milligrams per litre (mg/l). Acute lethal concentrations vary from 0.2 to 10.0 mg/l; chronic levels below about 0.63 mg/l produce no appreciable effects on minnow or bluegill populations.[1] The 1973 Water Quality Criteria suggest a maximum limit for linear alkyl sulfonates equal to 0.05 times the 96 hour Lethal Concentration (LC) 50 in the receiving water; such a level would correspond to about 0.2 mg/l. Practically all of the sulfonates (alkyl, alkyl phenyl, and naphthenic) are included as toxic substances on the National Institute for Occupational Safety and Health/Health, Education, and Welfare (NIOSH/HEW) list.[2] The toxicities seem to be rather low, however, as a high concentration is required before effects are noted.

Another effect results from the synergistic interaction of sulfonate surfactants with a number of known compounds comprising crude oil, facilitating the solubilization of

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[1] U.S. Environmental Protection Agency, Proposed Criteria for Water Quality, Vol. I, 1973, pp. 115-116.

[2] National Institute for Occupational Safety and Health/Health, Education, and Welfare, "Toxic Substances List," 1974.

TABLE 4-8

TERTIARY OIL RECOVERY

MINIMUM CONCENTRATION OF SURFACTANT REQUIRED TO PRODUCE A PERCEPTIBLE TASTE AND ODOR

SURFACE ACTIVE AGENT	MIN. CONC. (mg/l) TASTE	ODOR	TYPE OF TASTE OR ODOR
Alkyl aryl sulfonate	0.6	0.7	Limey, chemical
Alkyl aryl sulfonate	0.4	0.3	Soapy
Alkyl sulfate	3.0	0.2	Solvent
Alkyl sulfonate	1.4	0.3	Bitter, soapy, kerosene
Sulfonated amide	2.5	2.0	Chemical, soapy

Source: McKee and Wolf, Water Quality Criteria, for the California State Water Quality Control Board, 1963, p. 397.

toxic fractions of the crude oil.[1] Presumably, this affects the solubilization of organic toxicants by the sulfonates, with the result that penetration through epithelial barriers (e.g., the intestine) is facilitated.[2] Synergistic interactions have been reported with the carcinogen 3, 4 benzopyrene.[3] Though surfactants based on alkyl benzene sulfonates are not in common use today for tertiary recovery, it should be noted that these compounds are of concern because they do not break down biologically in sewage treatment plants, and can travel long distances in streams and through ground water without losing their identity. The more commonly used linear alkyl sulfonates are biodegradable; however, they are also two to four times more toxic.[4]

The compounds used in mobility control solutions such as polysaccharides, and most of the others listed on Table 4-2 are nontoxic. If discharged in excessive quantities, they contribute to the degradation of water quality mainly by increasing the biochemical oxygen demand (BOD) and to oxygen depletion in a receiving water body, and by serving as the basis of a rich nutrient medium which will encourage the growth of bacterial species. In typical micellar-polymer floods, very little of the materials will be returned to the surface. However, concentrations of 100 to more than 1,000 mg/l do occur in the produced water from simpler techniques of mobility control flooding with polymers alone.

Chemical hazards resulting from the use of hydrocarbon fractions other than crude oil in the micellar slug (Table 4-3) may be in the form of emulsified oils, or solutions of the water-soluble fractions of these oils. Due to cost considerations, crude oil has been the most common hydrocarbon constituent since it can easily be recovered from the produced fluids and requires little treatment prior to use. In special cases, other hydrocarbon fractions will be used. These fractions and the water soluble fractions of crude are of concern here. The aromatic hydrocarbons are the major group of acutely toxic compounds in oil residues. These also cause problems of fishtainting, and the production of unpleasant tastes and odors.[1] In addition, there is a potential carcinogenic problem associated with the introduction of ill-defined petroleum fractions into water supplies. The hydrocarbon compounds listed in Table 4-3 can cause tainting of the fish flesh and other aquatic organisms, and may be used in micellar-polymer flooding, thermal methods (Table 4-7b), and other tertiary recovery processes such as miscible hydrocarbon methods. In general, the hydrocarbons which may have some environmental impact are already utilized as biocides, lubricants, and corrosion inhibitors during primary and secondary oil recovery. Tertiary recovery would be expanding the amount, not changing the kind of chemical used.

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[1] McKee and Wolf, Water Quality Criteria, 1963, p. 397.

[2] National Academy of Sciences, Committee on Water Quality Criteria, Water Quality Criteria 1972, pp. 261-262.

[3] National Academy of Sciences, Water Quality Criteria 1972, p. 262.

[4] McKee and Wolf, Water Quality Criteria, 1963, p. 397.

Some of the electrolytes (Table 4-4) and compounds used in preflushing (Table 4-5) are potentially harmful, but the concentrations in micellar projects average less than 10.0 mg/l. Such a concentration is within the criteria for drinking water supplies.[2] Sodium nitrate and the inorganic phosphates are nutrients. If introduced in sufficient quantities, they can encourage the growth of undesirable algal slimes, and can accelerate the eutrophication of surface water bodies. Water turbidity can be increased, odors can be created, hydrogen sulfide gases can be produced by bacteria attacking abundant decaying matter, and a swampy taste can be imparted to the water. If introduced into groundwaters or surface waters which are used as the source of a drinking water supply, sodium nitrate can create further problems, since nitrates in drinking water have been linked rather convincingly to a high incidence of methemoglobenemia among the users (especially infants under three months of age) of the water supply.[3] The magnitude of this effect is, of course, extremely dependent upon the quantities of nitrates actually used. Therefore, the size of the project as well as the concentrations of electrolyte is important. Sodium sulfate is listed as a toxic substance, but only at extremely high concentrations which far exceed predicted levels in tertiary oil recovery processes. Subtoxic effects have been noted for sulfates, including imparting a "funny" taste and a slight laxative effect; but these, too, seem to be improbable at sulfate concentrations expected as a result of micellar-polymer flood.

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[1] EPA, Criteria for Water Quality, pp. 216-217

[2] EPA, Criteria for Water Quality, pp. 207-212.

[3] EPA, Criteria for Water Quality, pp. 208-209.

The cosurfactants used in micellar slugs are listed on Table 4-6. Isopropanol, isobutanol and amyl alcohol, are all toxic in high enough concentrations. But at the levels which may result from their escape from an oil reservoir, they should be degradable without too much difficulty by healthy ecosystems. In the normal course of things, they would travel along the usual catabolic pathways, being degraded by bacteria and contributing primarily to biochemical oxygen demand (BOD).

Two compounds mentioned as possible cosurfactants, phenol and cresol, would create significant water quality problems if introduced into ground or surface waters. Since these alcohols are much more dangerous in the environment, more expensive, and just as effective as the other alcohols, such compounds would appear to be the cosurfactants of last resort in tertiary oil recovery. However, shortages of the other alcohols may induce some substitution of phenol and cresol for micellar-polymer flood projects. The ortho-, meta- and para- forms of cresol, as well as phenol itself, are all listed as toxic substances on the NIOSH/HEW list.[1] The data on that list is limited, for the most part, to toxic effects on mammals (excluding man), so its usefulness to aquatic and human consumption problems might be questioned. Of somewhat more relevance is EPA's aquatic life toxicity data, which includes documented toxic effects on a number of first order organisms. Concentrations of 6.5 mg/l have been reported to cause extensive damage to trout reproductive systems, and concentrations of 1.0 mg/l are reported to have no toxic effects on trout.[2]

Death to humans exposed to acute phenol poisoning has occurred in periods as short as 30 minutes. Phenol can be absorbed through the intact skin. If death is not forthcoming, damage to the kidneys, liver, pancreas, spleen, and lungs may result. Skin absorption may eventually cause gangrene in the afflicted area. Chronic phenol poisoning is characterized by vomiting, difficulty in swallowing, excessive salivation, diarrhea, loss of appetite, nervous disorders and skin eruption.[3]

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[1] NIOSH/HEW, "Toxic Substances List," 1974.

[2] EPA, Criteria for Water Quality, p. 122.

[3] N. Irving Sax, Dangerous Properties of Industrial Chemicals (Van Nostrand Reinhold Co., 1968), p. 1007.

Phenol is reported to be a carcinogen, but it is difficult to extrapolate the mouse and guinea pig data used to support that conclusion to probable effects on human or aquatic life. Qualitatively, it is reasonable to expect some statistical carcinogenic effect in human populations exposed to phenol in their water supply.[1]

Effects other than direct toxic ones have been noted for those cosurfactants of last resort. Phenols impart unpleasant tastes and odors to water (with threshold odors being reported at 0.055 mg/l for para-cresol, 0.25 mg/l for meta-cresol, 0.26 mg/l for cresol, and 4.2 mg/l for phenol), and furthermore, they are not removed effectively by most conventional water treatment processes.[2] They can react with chlorine at public water supply disinfection plants to produce chlorophenolics, whose toxic effects, as well as effects on taste and odor, are much greater than those of phenols and cresols themselves (they are also more environmentally persistent than their parent phenolics). Phenol and cresol are biodegradable, though the rate of degradation is slow. Biochemical oxygen demand studies have shown that less than one-fifth of the phenols introduced into a seeded water sample are consumed within five days. Furthermore, phenol is a "tainting substance"; that is, it causes distinct unpleasant tastes in fish which have swum in waters containing them. Phenolic compounds, including cresol, have been reported to affect fish taste at the 0.001 mg/l levels.[3]

McKee and Wolf concluded, in 1963, that phenols in a concentration of 0.0001 mg/l would not interfere with domestic water supplies; in a concentration of 0.2 mg/l, they would not interfere with fish and aquatic life; at 50.0 mg/l, they would not interfere with irrigation; and at 1,000 mg/l, they would not interfere with livestock watering.[4] For most waters, the maximum recommended phenol concentration is 1.0 mg/l.

Most of the bacteriocides and biocides used in tertiary oil recovery listed on Table 4-9 are nonspecific, and display

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[1] See Section 4.2 for a discussion of carcinogenicity.

[2] EPA, Criteria for Water Quality, p. 223.

[3] EPA, Criteria for Water Quality, p. 143.

[4] McKee and Wolf, Water Quality Criteria, 1963, p. 240.

TABLE 4-9

TERTIARY OIL RECOVERY

CHEMICALS USED AS BACTERICIDES AND BIOCIDES[1]

- Aldehydes
  - Formaldehyde
  - Gluteraldehyde
  - Paraformaldehyde
- Alkyl phosphates
- Acetate salts of coco amines
- Alkyl amines
- Quaternary amines
  - Alkyl dimethyl ammonium chloride
  - Coco dimethyl benzyl ammonium chloride
- Diamine salts
  - Acetate salts of coco diamines
  - Acetate salts of tallow diamines
- Calcium sulfate
- Sodium hydroxide
- Heavy metal salts
- Chlorinated phenols
  - Alkyl dichlorophenol
  - Pentachlorophenol
  - Sodium salts of phenols
- Substituted phenols

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[1] T.J. Robichaux, "Bactercides Used in Drilling and Completion Operations," U.S. EPA Symposium on Environmental Aspects of Chemical Use in Well Drilling Operations, Houston, Texas, May 1965, p. 4.

significant toxicities to organisms other than the target bacteria. Although in many cases chlorination and adjustment in salinity and pH is often sufficient, these compounds may be more widely used to control bacteria which may attack surfactants and polymers used in a micellar-polymer flood. Toxic effects of most of them on aquatic life are well documented.[1] Aldehides have been reported to have TL 50 for fish of 50 to 400 mg/l.[2] Chlorinated phenols have a TL 50 for fish of 0.2 to 1.0 mg/l.[3] Quaternary amines have TL 50 for fish of 0.2 to 5.0 mg/l and other amines have a TL 50 for fish of 0.4 to 4.0 mg/l.[4] All of these compounds can be expected to be toxic to humans. Chlorinated hydrocarbons are stable in the environment, toxic to some wildlife and other non-target organisms, and have adverse physiological effects on man. They are stored in fatty tissues rather than being rapidly metabolized. Mild cases of poisoning cause headaches, dizziness, gastrointestinal disturbances, numbness, and weakness of the extremities, apprehension, and hyper-irritability. In severe cases, there are muscular fasciculations spreading from the head to the extremities, followed eventually by muscle spasms, leading in some cases to convulsions and death.[5] Chlorinated hydrocarbons are not completely removed by sewage treatment, nor by water purification plants.

Table 4-10 compares water quality criteria for various uses with the maximum concentrations of the chemicals which might be present in the oil reservoir. Two general conclusions may be drawn from these data. First, criteria are needed for many of the chemicals which may be used in tertiary oil recovery so that potential problems may be identified. Second, although the pathways from the oil reservoir to the water user involve low probabilities and large amounts of dilution and a number of coincidental chemical and physical occurences, the presence of some of

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[1] EPA, Criteria for Water Quality, pp. 241-304.

[2] McKee and Wolf, Water Quality Criteria, 1963, pp. 124, 191.

[3] Robichaux, "Bactericides Used in Drilling," p. 6.

[4] Robichaux, "Bactericides Used in Drilling," p. 6.

[5] National Academy of Sciences, Water Quality Criteria 1972, p. 76.

TABLE 4-10

TERTIARY OIL RECOVERY

COMPARISON OF CHEMICALS WHICH MAY BE PRESENT IN PROCESSES WITH WATER QUALITY CRITERIA

MATERIAL	WATER QUALITY CRITERIA[a]				MAXIMUM RESERVOIR WATER AFTER TERTIARY RECOVERY[b] (milligrams/liter)	PROCESS CODE[c]
	AI	AL	FW	WS		
Ditetradecyl dimethyl ammonium chloride	-	-	0.2 mg/l	0.5 mg/l	375 - 1900 mg/l	S
Dodecyl trimethyl ammonium chloride	-	-	0.2 mg/l	0.5 mg/l	375 - 1900	S
Hexadecyl trimethyl ammonium chloride	-	-	0.2 mg/l	0.5 mg/l	375 - 1900	S
Alkyl phenoxypolyethoxy ethanol	-	-	0.2 mg/l	0.5 mg/l	375 - 1900	S
p-Chloroaniline sulfate laurate	-	-	0.2 mg/l	0.5 mg/l	375 - 1900	S
p-Toluidene sulfate laurate	-	-	0.2 mg/l	0.5 mg/l	375 - 1900	S
Polyglycerol monolaurate	-	-	0.2 mg/l	0.5 mg/l	375 - 1900	S
Glycerol disulfoacetate monomyristate	-	-	0.2 mg/l	0.5 mg/l	375 - 1900	S
n-Methyltaurine oleamide	-	-	0.2 mg/l	0.5 mg/l	375 - 1900	S
Monobutylphenyl phenol sodium sulfate	-	-	0.2 mg/l	0.5 mg/l	375 - 1900	S
Polyoxyethelene alkyl phenol	-	-	0.2 mg/l	0.5 mg/l	375 - 1900	S
Morpholine stearate	-	-	0.2 mg/l	0.5 mg/l	375 - 1900	S
Pentaerythritol monostearate	-	-	0.2 mg/l	0.5 mg/l	375 - 1900	S
Dihexyl sodium succinate	-	-	0.2 mg/l	0.5 mg/l	375 - 1900	S
Diethyleneglycol sulfate	-	-	0.2 mg/l	0.5 mg/l	375 - 1900	S
n-Dodecyl-diethleneglycol sulfate	-	-	0.2 mg/l	0.5 mg/l	375 - 1900	S
Sodium glyceryl monolaurate sulfate	-	-	0.2 mg/l	0.6 mg/l	375 - 1900	S
Sodium sulfate oleylethydanilide	-	-	0.2 mg/l	0.5 mg/l	375 - 1900	S
Alphaolefin sulfonate	-	-	0.2 mg/l	0.5 mg/l	375 - 1900	S

[a] AI = agricultural (irrigation); AL = agricultural (livestock); FW = fresh water; WS = water supply.

[b] Tables 2-6 through 2-9.

[c] S = surfactant; C = cosurfactant; P = mobility control; B = bactericide; E = electrolyte; H = hydrocarbon in slug; T = thermal methods; N = naturally occuring in oil; G = gas injection.

TABLE 4-10 (CONT.)

MATERIAL	WATER QUALITY CRITERIA AI	AL	FW	WS	MAX. RESERVOIR WATER AFTER TERTIARY RECOVERY (mg/1)	PROCESS CODE
Alkyl aryl sulfonate detergent	-	-	0.2 mg/1	0.5 mg/1	375 - 1900	S
Alkyl aryl napthenic sulfonate	-	-	0.2 mg/1	0.5 mg/1	375 - 1900	S
Hexadecylnapthalene sulfonate	-	-	0.2 mg/1	0.5 mg/1	375 - 1900	S
Sodium lauryl sulfonate	-	-	0.2 mg/1	0.5 mg/1	375 - 1900	S
Triethanolamine laurate	-	-	0.2 mg/1	0.5 mg/1	375 - 1900	S
Triethanolamine myristate	-	-	0.2 mg/1	0.5 mg/1	375 - 1900	S
Triethanolamine oleate	-	-	0.2 mg/1	0.5 mg/1	375 - 1900	S
Fusel oil	-	-	-	-	200 - 4000	C
Phenol	-	-	<1 mg/1[a]	1 µg/1	200 - 4000	C
p-Nonyl phenol	-	-	-	1 µg/1	200 - 4000	C
Isopentanol	-	-	-	-	200 - 4000	C
2-pentanol	-	-	-	-	200 - 4000	C
Cresol	-	-	<0.07 mg/1[a]	1 µg/1	200 - 4000	C
Decyl alcohols	-	-	-	-	200 - 4000	C
Ethanol	-	-	-	-	200 - 4000	C
Isobutanol	-	-	-	-	200 - 4000	C
n-Butanol	-	-	-	-	200 - 4000	C
Cyclohexanol	-	-	-	-	200 - 4000	C
1-Hexanol	-	-	-	-	200 - 4000	C
2-Hexanol	-	-	-	-	200 - 4000	C
1-Octanol	-	-	-	-	200 - 4000	C
2-Octanol	-	-	-	-	200 - 4000	C

[a] Tainting substance

TABLE 4-10 (CONT.)

MATERIAL	WATER QUALITY CRITERIA AI	AL	FW	WS	MAX. RESERVOIR WATER AFTER TERTAIRY RECOVERY (mg/l)	PROCESS CODE
Isopropanol	-	-	-	-	200 - 4000	C
Formaldehyde	-	-	-	-	200 - 4000	B/C
Gluteraldehyde	-	-	-	-	200 - 4000	B/C
Paraformaldehyde	-	-	-	-	200 - 4000	B/C
Amides	-	-	-	-	200 - 4000	C
Amino compounds	-	-	-	-	200 - 4000	C
Sorbitan fatty ester	-	-	-	-	200 - 4000	C
Ketones	-	-	-	-	200 - 4000	C
Alkylated aryl compounds	-	-	(no odor or visible film)	(no odor or visible film)	950 - 11250	H
Anthenic compounds	-	-	(no odor or visible film)	(no odor or visible film)	950 - 11250	H
Alkyl phenols	-	-	<1 mg/l	(no odor or visible film)	950 - 11250	H
Benzene	-	-	(no odor or visible film)	(no odor or visible film)	950 - 11250	H
Toluene	-	-	<0.25 mg/l[a]	(no odor or visible film)	950 - 11250	H/T
Crude oil (sour)	-	-	(no odor or visible film)	(no odor or visible film)	950 - 11250	H
Crude oil (sweet)	-	-	(no odor or visible film)	(no odor or visible film)	950 - 11250	H

[a] Tainting substance

TABLE 4-10 (CONT.)

MATERIAL	WATER QUALITY CRITERIA AI	AL	FW	WS	MAX. RESERVOIR WATER AFTER TERTIARY RECOVERY (mg/l)	PROCESS CODE
Overheads from crude columns	-	-	(no odor or visible film)	(no odor or visible film)	950 - 11250	H
Side cuts from crude columns	-	-	(no odor or visible film)	(no odor or visible film)	950 - 11250	H
Gas oils	-	-	(no odor or visible film)	(no odor or visible film)	950 - 11250	H
Straight run gasoline	-	-	(no odor or visible film)	(no odor or visible film)	950 - 11250	H
Karosene	-	-	<0.1 mg/l[a]	(no odor or visible film)	950 - 11250	H
Liquified petroleum gas	-	-	(no odor or visible film)	(no odor or visible film)	950 - 11250	H
Napthas	-	-	(no odor or visible film)	(no odor or visible film)	950 - 11250	H
Heavy napthas	-	-	(no odor or visible film)	(no odor or visible film)	950 - 11250	H
Decane	-	-	(no odor or visible film)	(no odor or visible film)	950 - 11250	H
Dodecane	-	-	(no odor or visible film)	(no odor or visible film)	950 - 11250	H

[a] Tainting substance

TABLE 4-10 (CONT.)

MATERIAL	WATER QUALITY CRITERIA AI	WATER QUALITY CRITERIA AL	WATER QUALITY CRITERIA FW	WATER QUALITY CRITERIA WS	MAX. RESERVOIR WATER AFTER TERTIARY RECOVERY (mg/l)	PROCESS CODE
Heptane	-	-	(no odor or visible film)	(no odor or visible film)	950 - 11250	H
Octane	-	-	(no odor or visible film)	(no odor or visible film)	950 - 11250	H
Pentane	-	-	(no odor or visible film)	(no odor or visible film)	950 - 11250	H
Propane	-	-	(no odor or visible film)	(no odor or visible film)	950 - 11250	H
Cyclohexane	-	-	(no odor or visible film)	(no odor or visible film)	950 - 11250	H
Tip top crude	-	-	(no odor or visible film)	(no odor or visible film)	950 - 11250	H
Synthesized hydrocarbons	-	-	(no odor or visible film)	(no odor or visible film)	950 - 11250	H
Diapthenic compounds	-	-	<0.1 mg/l[a]	(no odor or visible film)	950 - 11250	H
Amines	-	-	-	-	5 - 100	P

[a] Tainting substance

TABLE 4-10 (CONT.)

MATERIAL	WATER QUALITY CRITERIA				MAX. RESERVOIR WATER AFTER TERTIARY RECOVERY (mg/1)	PROCESS CODE
	AI	AL	FW	WS		
Carboxymethylcellulose	-	-	-	-	5 - 100	P
Carboxyvinyl polymer	-	-	-	-	5 - 100	P
Desoxyribonucleic acid	-	-	-	-	5 - 100	P
Glycerin	-	-	-	-	5 - 100	P
Polyacrilamide	-	-	-	-	5 - 100	P
Polyethene oxide	-	-	-	-	5 - 100	P
Polyisobutylene in benzene	-	-	-	-	5 - 100	P
Polysaccharide	-	-	-	-	5 - 100	P
Rheopectic polymer	-	-	-	-	5 - 100	P
Rubber in benzene	-	-	-	-	5 - 100	P
Starch	-	-	-	-	5 - 100	P
Aldoses B series	-	-	-	-	5 - 100	P
Aldoses L series	-	-	-	-	5 - 100	P
Dextrans	-	-	-	-	5 - 100	P
Ketoses B series	-	-	-	-	5 - 100	P
Ketoses L series	-	-	-	-	5 - 100	P
Conjugated saccarides	-	-	-	-	5 - 100	P
Disaccharides	-	-	-	-	5 - 100	P
Monosaccharides	-	-	-	-	5 - 100	P
Polysaccharidos	-	-	-	-	5 - 100	P
Tetrasaccharidos	-	-	-	-	5 - 100	P

TABLE 4-10 (CONT.)

MATERIAL	WATER QUALITY CRITERIA				MAX. RESERVOIR WATER AFTER TERTIARY RECOVERY (mg/l)	PROCESS CODE
	AI	AL	FW	WS		
Hydrazine	-	-	-	-		T
Hydrogen peroxide	-	-	-	-		T
Quinoline	-	-	<0.5 mg/l^a	(no odor or visible film)		T
Sodium hydroxide	-	-	-	-		E
Quaternary ammonium salts	-	-	-	-		E
Fluoride solutions	2 mg/l	2 mg/l	-	-		E
Potassium permanganate	-	-	-	-		E
Sodium hydroxide	-	-	-	-		E
Polyacrylates	-	-	-	-		E
Inorganic phosphates	-	-	-	no limit		E
Organic phosphates	-	-	-	no limit		E
Organic phosphonates	-	-	-	-		E
Acetate salts of coco amines	-	-	-	-		B
Quaternary amines	-	-	-	-		B
Octyl phenoxy polyethoxy alcohol	-	-	0.2 mg/l	0.5 mg/l	375 - 1900	S
Oxyalkylated sulfated alcohol	-	-	0.2 mg/l	0.5 mg/l	375 - 1900	S
Modified ester alcohol sodium salt	-	-	0.2 mg/l	0.5 mg/l	375 - 1900	S
Ethylene cycloamido lauryl, 2-hydroxy ethelene sodium alcoholate methylene carboxylate	-	-	0.2 mg/l	0.5 mg/l	375 - 1900	S
Modified fatty alkylolmide	-	-	0.2 mg/l	0.5 mg/l	375 - 1900	S
Alkyl amido betane	-	-	0.2 mg/l	0.5 mg/l	375 - 1900	S

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[a] Tainting substance

TABLE 4-10 (CONT.)

MATERIAL	WATER QUALITY CRITERIA AI	AL	FW	WS	MAX. RESERVOIR WATER AFTER TERTIARY RECOVERY (mg/l)	PROCESS CODE
c-Cetyl betane	-	-	0.2 mg/l	0.5 mg/l	375 - 1900	S
Coconut diethanolamide	-	-	0.2 mg/l	0.5 mg/l	375 - 1900	S
Diethanolamine superamide	-	-	0.2 mg/l	0.5 mg/l	375 - 1900	S
Lauric acid diethanolamine condensate	-	-	0.2 mg/l	0.5 mg/l	375 - 1900	S
Alkyl aryl polyethenoxy ester	-	-	0.2 mg/l	0.5 mg/l	375 - 1900	S
Alkyl polyethieneoxy ethanol	-	-	0.2 mg/l	0.5 mg/l	375 - 1900	S
Polyoxyetholene alkylaryl ether	-	-	0.2 mg/l	0.5 mg/l	375 - 1900	S
Condensation product of ethylene oxide with propylene glycol	-	-	0.2 mg/l	0.5 mg/l	375 - 1900	S
Fatty alcohol alkyloamine sulfate	-	-	0.2 mg/l	0.5 mg/l	375 - 1900	S
Modified ammonium alkyl sulfate	-	-	0.2 mg/l	0.5 mg/l	375 - 1900	S
Sodium hydrocarbon sulfonate	-	-	0.2 mg/l	0.5 mg/l	375 - 1900	S
Sodium lauryl sulfonate	-	-	0.2 mg/l	0.5 mg/l	375 - 1900	S
Antimony	-	-	-	1.0 mg/l	0.05	N/T/G
Arsenic	0.10 mg/l	0.2 mg/l	-	0.1 mg/l	<0.12	N/T/G
Barium	-	-	-	1.0 mg/l	<0.14	N/T/G
Manganese	0.2 mg/l	no limit	-	0.05 mg/l	<0.05	N/T/G
Nickel	0.2 mg/l	-	0.02 x 96-hr. LC50	-	77	N/T/G
Tin	-	-	-	-	<1.0	N/T/G
Vanadium	-	0.1 mg/l	-	-	48	N/T/G

these materials at concentrations three orders of magnitude greater than acceptable water quality criteria in abandoned oil fields is a difficult problem in environmental protection for the future. The actual scale of the problem will vary from region to region depending on factors affecting the risk of releasing these chemicals and the proximity of important aquifers or water bodies to oil reservoirs.

4.1.1 Compounds and Degradation Products

Although many of the chemicals used in tertiary oil recovery processes may form degradation products, such degradation occurs only under extreme conditions of pressure and temperature. For example, typical conditions in a reservoir where micellar flooding is undertaken are estimated to be: pH of 6-8; temperatures up to 200° F; pressures up to 3,000 pounds per square inch. Degradation occurs most easily at more acidic (pH=3) or more alkaline (pH=11) conditions, with temperature in excess of 250° F; and pressures in excess of 3,000 pounds per square inch.

In addition to the affect of these reservoir conditions on the degradation process, there may be effects due to the other compounds in the formation matrix and their interaction. A chemical used in a micellar-polymer flood may be the limiting factor in a degradation reaction (e.g., it must be present for the reaction to occur), or it may serve as a catalyst for the degradation reaction (e.g., it affects the rate of the reaction).

The descriptions of toxic effects of chemicals and their associated degradation products is based upon Dangerous Properties of Industrial Materials, by N. Irving Sax, Third Edition, 1968. Definitions of the toxic effects are at the end of Table 4-10. Due to the nature of the reactions and the possible pathways for these pollutants, "major chronic systemic" effects are considered most problematic.

The surfactants used in tertiary oil recovery processes are a very important group of chemicals because the sulfonation reaction by which most are manufactured is reversible. Table 4-11 lists some degradation reactions which may occur and the toxicity of the accompanying reaction products. Ditetradecyl dimethyl ammonium chloride is probably stable, although it may undergo degradation to 1-tetradecene and

TABLE 4-11

POSSIBLE DEGRADATION REACTIONS OF MATERIALS PROPOSED FOR USE IN TERTIARY OIL RECOVERY

CHEMICAL	TOXICITY	REACTION	DEGRADATION PRODUCTS	TOXICITY
Ditetradecyl dimethyl ammonium chloride	Unknown	Elimination	a) 1-Tetradecene	a) Unknown
			b) Dimethyl-tetradecyl ammonium chloride	b) Unknown
Dodecyl trimethyl ammonium chloride	Unknown	Elimination	a) 1-Dodecene	a) Unknown
			b) Trimethyl ammonium chloride	b) Unknown
Hexadecyl trimethyl ammonium chloride	Unknown	Elimination	a) 1-Hexadecene	a) Unknown
			b) Trimethyl ammonium chloride	b) Unknown
Alkyl phenoxy polyethoxy ethanol	Unknown	Hydrolysis	a) Glycol	a) No acute local Major acute systemic Minor chronic local Minor chronic systemic
p-Chloroaniline sulfate laurate	Unknown	Desulfonation and Hydrolysis	a) p-Chloroaniline	a) Minor acute local Lethal acute systemic Minor chronic local Lethal chronic systemic
			b) Sulfuric acid	b) Lowers pH
			c) Lauric acid	c) Unknown
p-Toluidine sulfate laurate	Unknown	Desulfonation and Hydrolysis	a) p-Toluidine	a) Major acute local Lethal acute systemic Minor chronic local Major chronic systemic
			b) Sulfuric acid	b) Lowers pH
			c) Lauric acid	c) Unknown
Polyglycerol monolaurate	Unknown	Hydrolysis	a) Polyglycerol	a) Unknown
			b) Lauric acid	b) Unknown
Glycerol disulfo-acetate monomyristate	Unknown	Desulfonation	a) Glycerol diacetate monomyristate	a) Unknown
			b) Sulfate ion	b) Laxative

TABLE 4-11 (CONT.)

CHEMICAL	TOXICITY	REACTION	DEGRADATION PRODUCTS	TOXICITY
Monobutyl phenyl phenol sodium sulfate	Unknown	Hydrolysis	a)Sulfate ion b)Monobutyl phenyl phenol	a)Laxative b)Unknown
Polyoxyethylene alkyl phenol	Unknown	Hydrolysis	a)Glycol	a)No acute local Major acute systemic Minor chronic local Minor chronic systemic
Morpholene stearate	Unknown	Hydrolysis	a)Morpholene b)Stearic acid	a)Major acute local Major acute systemic Unknown chronic local Unknown chronic systemic b)Slight
Pentaerythriol monostearate	Unknown	Hydrolysis	a)Pentaerythriol b)Steric acid	a)Unknown b)Slight
Gihexyl sodium succinate				
Diethyleneglycol sulfate	Unknown	Hydrolysis	a)Ethylene glycol b)Sulfuric acid	a)No acute local Major acute systemic Minor chronic local Minor chronic systemic b)Lowers pH
n-Dodecyl-diethylene glycol sulfate	Unknown	Hydrolysis	a)Sulfate ion b)n-Dodecyl-diethylene glycol	a)Laxative b)Unknown
Sodium glyceryl monolauryl sulfate	Unknown	Desulfonation	a)Glyceryl monolaurate b)Sulfate ion	a)Unknown b)Laxative
Alpha olefin sulfonates	Unknown	Desulfonation	a)Hydrocarbon b)Sulfate ion	a)Varies (irritant) b)Laxative
Alkyl aryl sulfonate detergent	Unknown	Desulfonation	a)Hydrocarbon b)Sulfate ion	a)Varies (irritant) B)Laxative
Alkyl aryl naphthenic sulfonate	Unknown	Desulfonation	a)Alkyl aryl naphthalene b)Sulfate ion	a)Unknown b)Laxative

TABLE 4-11 (CONT.)

CHEMICAL	TOXICITY	REACTION	DEGRADATION PRODUCTS	TOXICITY
Hexadecyl naphthalene sulfonate	Unknown	Desulfonation	a)Hexadecyl naphthalene b)Sulfate ion	a)Unknown b)Laxative
Sodium lauryl sulfonate	Unknown	Hydrolysis	a)Lauryl alcohol b)Sulfate ion	a)Unknown b)Unknown
Triethanolamine laurate	Unknown	Hydrolysis	a)Triethanolamine b)Lauric Acid	a)No acute local Minor acute systemic No chronic local Minor chronic systemic b)Unknown
Triethanolamine myristate	Unknown	Hydrolysis	a)Triethanolamine b)Myristic acid	a)No acute local Minor acute systemic No chronic local Minor chronic systemic b)Unknown
Triethanolamine oleate	Unknown	Hydrolysis	a)Triethanolamine b)Oleic acid	a)No acute local Minor acute systemic No chronic local Minor chronic systemic b)Minor acute local Unknown acute systemic Unknown chronic local Minor chronic systemic
Toluene		Stable		Major acute local Major acute systemic Minor chronic local Major chronic systemic
Alkyl phenols	Probable High	Stable		
Esters	Low to High	Hydrolysis	a)Acid b)Alcohol	
Aldehydes	Unknown	Oxidation		Major acute local Lethal acute systemic Major chronic local Unknown chronic systemic

TABLE 4-11 (CONT.)

CHEMICAL	TOXICITY	REACTION	DEGRADATION PRODUCTS	TOXICITY
Ketones	Unknown	Stable		
Alcohols	Minor	Stable		
p-Nonyl phenol	Unknown	Stable		
Quaternary amines	Toxic	Elimination	Tertiary amine	Toxic
Mobility buffers	Not toxic	Stable		
Mercuric chloride	Very toxic	Stable		
Hydrazine	Explosive Lethal			
Quinoline	Paralysis	Stable		

[a] Definitions of Degree of Toxicity: (N. Irving Sax, Dangerous Properties of Industrial Materials, Third Edition, 1968, p. 2)

Minor:

Acute local = materials which on single exposures lasting seconds, minutes or hours cause only slight effects on the skin or mucous membranes regardless of the extent of the exposure.

Acute systemic = materials which can be absorbed into the body by inhalation, ingestion or through the skin and which produce only slight effects following single exposures lasting seconds, minutes, or hours, or following ingestion of a single dose, regardless of the quantity absorbed or the extent of exposure.

Chronic local = materials which on continuous or repeated exposures extending over periods of days, months, or years cause only slight harm to the skin or mucous membranes. The extent of exposure may be great or small.

Chronic systemic = Materials which can be absorbed into the body by inhalation, ingestion or through the skin and which produce only slight effects following continuous or repeated exposures extending over days, months or years. The extent of the exposure may be great or small. In general, those substances classified as having "slight toxicity" produce changes in the human body which are readily reversible and which will disappear following termination of exposure, either with or without medical treatment.

Major:

Acute local = materials which on single exposures lasting seconds or minutes cause injury to skin or mucous membranes of sufficient severity to threaten life or to cause permanent physical impairment or disfigurement.

Acute systemic = materials which can be absorbed into the body by inhalation, ingestion or through the skin and which can cause injury of sufficient severity to threaten life following a single exposure lasting seconds, minutes or hours, or following ingestion of a single dose.

Chronic local = materials which on continuous or repeated exposures extending over periods of days, months or years can cause injury to skin or mucous membranes of sufficient severity to threaten life or to cause permanent impairment, disfigurement or irreversible change.

Chronic systemic = materials which can be absorbed into the body by inhalation, ingestion or through the skin and which can cause death or serious physical impairment following continuous or repeated exposures to small amounts extending over periods of days, months or years.

dimethyl-tetradecyl ammonium chloride. The toxicity of 1-tetradecene is unknown, although it is a probable irritant with narcotic effects at very high concentrations. Dodecyl trimethyl ammonium chloride is probably stable, with possible decomposition to 1-dodecene and trimethyl ammonium chloride. The details of the toxicity of dodecene are unknown, although it is a probable irritant and narcotic in high concentrations. Hexadecyl trimethyl ammonium chloride is probably stable, with the possible degradation to 1-hexadecene and trimethyl ammonium chloride. The toxicity of 1-hexadecene is unknown. Alkyl phenoxy poly-ethoxy ethanol may hydrolyze to glycol. One hundred millilitres of ethylene glycol is reported to be the lethal dose for man in an acute dose. If ingested, glycol causes initial central nervous system stiumlation, followed by depression. Later, it causes kidney damage which can terminate fatally. Para-chloraniline sulfate laurate is probably stable, with a possible desulfonation and hydrolysis to para-chloraniline, sulfuric acid, and lauric acid. Para-chloraniline can produce severe systemic disturbance. Symptoms produced include headache, weakness, difficulty in breathing, air hunger, psychic disturbances, and marked irritation of the kidneys and bladder. This compound can be absorbed through the intact skin. Para-toluidine sulfate laurate is probably stable, with a possible desulfonation and hydrolysis to paratoluidine, sulfuric acid, and lauric acid. Although the details concerning the toxicity of lauric acid are unknown, animal data suggest low toxicity for lauric acid esters. There is some evidence indicating that paratoluidine is an irritant, an allergen, and can show toxic effects if ingested. Polyglycerol mono-laurate is probably stable, with the possible hydrolysis to polyglycerol and lauric acid. Glycerol disulfoacetate monomyristate is probably stable, with possible desulfonation to glycerol diacetate monomyristate and a sulfate ion. Mono butyl phenyl phenol sodium sulfate is probably stable, with the possible degradation to sulfate ion and mono butyl phenol. Details concerning the toxicity of mono butyl phenyl phenol sodium sulfate are unknown. The epoxy units of polyoxyethylene alkyl phenol may hydrolyze to glycol.

Morpholene stearate may undergo hydrolysis to morpholene and stearic acid. Morpholene is irritating to skin, eyes, and mucous membranes, and has produced kidney damage in experimental animals. However, it is also used as a food additive for human consumption. Stearic acid has only slight toxicity, and is a substance which migrates to food from packaging materials. Pentaerythritol monostearate is probably stable, with possible hydrolysis to pentaerythritol and stearic acid. The toxicity of pentaerythritol is unknown. Dihexyl sodium succinate is probably stable, with possible copolymerization with polyfunctional alcohols or amines.

Diethyleneglycol sulfate is probably stable, with possible hydrolysis to ethylene glycol and sulfuric acid. N-dodecyl diethylene glycol sulfate is probably stable, with possible degradation to sulfate ion and n-dodecyl diethylene glycol. Sodium glyceryl monolauryl sulfate is probably stable, with possible desulfonation to glyceryl monolaurate and sulfate ion. Alpha-olefin sulfonates may suffer possible desulfonation to a hydrocarbon and a sulfate ion. The same degradation process may occur to alkyl aryl sulfonate detergents. Alkyl aryl naphthenic sulfonates are probably stable, with a possible desulfonation to alkyl aryl naphthlene and a sulfate ion. Hexadecyl naphthlene sulfonate is probably stable, with possible desulfonation to hexadecyl naphthlene and a sulfate ion. Sodium lauryl sulfonate is probably stable, with a possible decomposition to lauryl alcohol and sulfate ion. Lauryl alcohol (also known as 1-dodecanol) is relatively insoluble in water, and has unknown toxicity. Limited animal experiments indicate low toxicity for lauryl alcohol. Triethanol amine laurate may undergo hydrolysis to form triethanol amine and lauric acid. Triethanol amine exhibits low toxicity, though liver and kidney damage have been demonstrated in animals under chronic exposure. Triethanol amine myristate is probably stable, with possible hydrolysis to triethanol amine and myristic acid. Triethanol amine oleate is probably stable, with possible hydrolysis to triethanol amine and oleic acid. Oleic acid has low toxicity.

Among the cosurfactants, ketones and para-nonyl phenols are both stable, as are isopropanol, n-butanol isobutanol, 1-hexanol, 2-hexanol, 2-pentanol, and cyclohexanol. Esters may hydrolyze to an acid and an alcohol. Aldehydes are probably stable, although they may be oxidized by strong oxidizing agents.

Quarternary amines (used as corrosion inhibitors) may eliminate the longest side chain to form a tertiary amine.

Most of the other chemicals used in tertiary oil recovery are very stable. All mobility buffers appear to be stable. Mercuric chloride (a biocide) is stable, and would stay in solution in all but extreme pH increases. Quinoline used to ignite in-situ combustion is stable. However, hydrazine also used to ignite in-situ combustion is a very strong reducing agent, and will probably be converted to N_2 with a transfer of its hydrogen atoms to other molecules.

Of the degradation reactions which may occur, hydrolysis and desulfonation of surfactants such as polyoxyethylene alkyl phenol, diethyleneglycol sulfate, alkyl phenoxy polyethoxy ethanol to glycol and p-chloroanaline sulfate laurate to p-chloroaniline are the potential largest hazards.

4.2 Carcinogenicity of Chemicals

A number of the chemicals proposed for use in tertiary oil recovery operations have been shown either to induce the formation of tumors in experimental animals or to accelerate the induction of such tumors by other chemical carcinogens.[1] Table 4-12 summarizes the major carcinogenic chemicals which may be used. A number of caveats apply to estimating the carcinogenic risk associated with tertiary oil recovery operations:

- The experiments used to demonstrate the carcinogenicity of particular chemicals are frequently carried out at rather high dosages. For example, a recent study[2] demonstrated the induction of mammary, lung, and lymph tumors resulting from the force feeding of mice with a 43 percent solution of ethyl alcohol over the course of 1,020 days. Although this constitutes technical evidence of carcenogenicity, its relevance to the effects of ethyl alcohol at normal dosage levels is questionable.

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[1] Documentation of these effects can be found in the Department of Health, Education and Welfare's "Request for Information on Certain Chemicals," (Federal Register 40 (121): 26390ff (1975)), which lists a set of chemicals identified by the NIOSH as having "reportedly produced an observed or suspected carcinogenic response in anaimals, based upon published articles in the literature," and in HEW's "Survey of Compounds which have been Tested for Carcinogenic Activity," which summarizes the recent literature on carcinogenic properties of chemicals.

[2] M. Kuratsune et al., Gann. 62, (1971): 395-405.

TABLE 4-12

TERTIARY OIL RECOVERY

CARCINOGENIC CHEMICALS WHICH MAY BE USED IN TERTIARY OIL RECOVERY OPERATIONS

Surfactants (possibility of synergistic interactions with organic carcinogens)

Alkyl aryl sulfonates

Carboxymethylcellulose

Benzene and benzene derivatives

Polycyclic hydrocarbons

Crude oil and crude oil fractions

Formaldehyde and paraformaldehyde

Phenol and phenol derivatives

- The literature (except in infrequent epidemiological studies of occupational or air pollution related carcinogenesis) deals almost exclusively with studies performed on experimental animals. Although *a priori* considerations lead one to suspect that a substance which is carcinogenic in mice and hamsters is probably carcinogenic in humans, procedures are needed to determine how to extrapolate from animal data to humans.
- Even within individual species, dose-response relationships for chemical carcinogens are not well documented. On the basis of the literature, it is only possible to make qualitative statements regarding the human carcinogenicity of a particular chemical.
- The literature on chemical carcinogenisis is highly variable with respect to dosage, degree of control, and type of system used (e.g., testing for introduction of tumors in various mammalian species as opposed to assaying cell transformation *in vitro*).

Thus, it is almost impossible to make valid quantitative assessments of the human carcinogenic risk associated with the use of various chemicals. In recognition of this fact, the U.S. Environmental Protection Agency has recently defined nine principles to be used in guiding policy making with regard to the regulation of carcinogenic chemicals.[1] Many of these guidelines are relevant to the problem of assessing the risks associated with the use of carcinogens in tertiary oil recovery operations:

1. "A carcinogen is any agent that increases tumor--benign or malignant--induction in man and animals..."
2. "Carcinogenesis is characterized by its irreversibility and long latency period following initial exposure to the carcinogenic agent..."
3. "There is great variability in individual susceptibility to carcinogens..."

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[1] *Chemical and Engineering News*, November 3, 1975, p. 17.

4. "The concept of a 'threshold' exposure level for a carcinogenic agent has no practical significance because there is no valid method of establishing such a level..."

5. "A carcinogenic agent may be identified through analysis of tumor induction results with laboratory animals exposed to the agent, or on a post hoc basis by properly conducted epidemiological studies..."

6. "Any substance that produces tumors in animals must be considered a carcinogenic hazard to man if the results were achieved according to the established parameters of a valid carcinogenesis test..."

The central thrust of these principles is to broaden considerably the definition of "carcinogen" (e.g., to include materials which have been shown to induce benign tumors) and to assert that in the absence of meaningful procedures to quantitatively determine human carcinogenic dose/response relationships or thresholds, it is necessary to consider as carcinogenic any chemicals which have been shown to induce tumors, at any dosage, in any experimental animal. A positive carcinogenic risk is considered to exist no matter how low the concentration of the substance in the environment; so that threshold levels, such as have been set up for various pesticides and other toxic substances in surface water bodies,[1] cannot be set up. In terms of the subject of this report, this means that attention should be given to any chemical which has shown carcinogenic effects in some system, no matter what the actual concentrations may be in the vicinity of a tertiary oil recovery project. This is the approach which has been adopted in this section.

Of the chemical surfactants listed in Table 4-1, carcinogenic effects are only indicated for the alkyl aryl sulfonates, alkyl benzene sulfonates and some derivatives of alkyl naphthenic sulfonates. However, the synergistic interactions of otherwise non-carcinogenic surfactants with other chemicals will probably prove to be more important than any direct carcinogenic effects they may produce. Alkyl benzene sulfonates, for example, have rather low carcinogenicities when administered alone, but they have been found to increase the tumor-inducing properties of 4-nitroquinoline-1-oxide.[1] This effect is presumably due to the solubilization of the carcinogen by the sulfonate, and it may also be produced by other surfactants.

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[1] See, for example, EPA, Criteria for Water Quality, 1975.

Among the mobility buffers, carboxymethylcellulose, polyethylene oxide (polyethylene glycol), dextran, and benzene are suspected carcinogens.[2] High long-term doses of glycerin (glycerol) are also indicated as being tumorigenic.

"Crude oil" (as petroleum) is listed as a suspected carcinogen, and some carcinogenic activity remains in its purified fractions such as oil, which is listed as a carcinogen. Benzene is also a carcinogen, as are certain of the benzene derivatives such as toluene, which is sometimes used in stimulating wells prior to thermal methods of oil recovery. A further danger exists that these compounds may interact with chlorine in drinking water disinfection plants to produce carcinogenic chlorinated aromatics. Extensive data exists documenting the carcinogenicity of polycyclic hydrocarbons (including benzpyrene and some of the naphthenics).[3,4] Several alkylated aryl compounds, as well as their chlorination products, are included in the references. Pure paraffinics and cycloparaffinics seem to be relatively non-carcinogenic.

The only potential carcinogen listed among electrolytes is the category "organic acids," but inorganic salts are most commonly used. More specific information will be needed about the organic acids used in order to assess the carcinogenicity of these compounds. No known carcinogens are listed for preflushing chemicals.

Definite evidence exists supporting the carcinogenicity of cosurfactants such as formaldehyde, paraformaldehyde, and phenol, but these materials are not most commonly used. No evidence exists for the carcinogenicity of pure preparations of most of the organic alcohols, except for one or two, such as ethanol, which are carcinogenic at extremely high doses administered over long time periods. More information will be needed on which amides, amino compounds or ketones are used.

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[1] Takahashi, Gann. 61(1), (1970): 27-33.

[2] U.S. Department of Health, Education and Welfare, "Request for Information on Certain Chemicals," Federal Register 40 (121):26391ff (1975).

[3] HEW, "Certain Chemicals, 1975.

[4] U.S. Department of Health, Education and Welfare, Survey of Compounds Which Have Been Tested for Carcinogenic Activity, 1971.

CHAPTER FIVE

EFFECTS OF TERTIARY OIL RECOVERY ON GROUNDWATER

5.0 Introduction

The chemicals used in tertiary oil recovery which may be dissolved or entrained in water produced by the process are of environmental concern because these chemicals may enter and contaminate groundwater supplies. This chapter reviews the possible causes of groundwater pollution which may be affected by tertiary oil recovery methods.

Primary contamination of groundwater results in large part from leaks in well casings and from seepage through the walls of waste disposal pits. Pollution from lined pits is rare but may have longlasting effects if brine has escaped to permeable sands outside the lining. Direct contamination of surface water can occur from spills or seeps to the surface of chemicals, water or brines, or oil. Since most water bodies flow eventually into others, pollution usually affects more than the first body it enters. Additionally, contaminants on the land may be washed by rain into surface water systems. In all cases, pollution will continue as long as contaminants remain and water supplies are exposed -- perhaps long after production and disposal operations have ceased.

The problems of spills, surface seeps and pipeline breaks have been recognized as a result of conventional oil extraction operations. Regulations regarding impervious linings for brine pits are an example of this awareness. Because of close supervision, monitoring and modification and upgrading of equipment, it is hoped that the likelihood of leaks and spills during a tertiary oil recovery project will be less than conventional operations. However, during the recovery activity and after it is completed it is possible for leaks to occur. Most important to understand are the ways in which water soluble chemicals introduced into an oil-bearing strata for tertiary recovery may escape unseen into an aquifer. The risks of leakage of these chemicals due to failure of a well will be determined by analyzing the problems historically associated with oil production and judging what additional or different effects may result from tertiary oil recovery activity.

This chapter will address these issues in three stages. The first will establish the conceptual framework of the problem. The second will examine the accident record of a representative oil-producing region -- the Texas Upper Gulf Coast (District III of the Texas Railroad Commission) -- to provide some first-order estimates of the probability of contamination from tertiary recovery projects. In the third section the relative risk levels of the tertiary oil recovery methods will be determined qualitatively for each region. This approach provides an initial appraisal of the relevant risk factors. The modelling of regional groundwater systems and computation of the probabilities of well failure region-by-region are required to understand fully the risks of tertiary oil recovery.

5.1 Mechanisms of Contamination

5.1.1 Hydrology

Groundwater is held in permeable layers of sand (aquifers) separated from each other and from the surface by less permeable layers of rock, or by impermeable layers (aquicludes). Freshwater (less than 1,000 mg/l total dissolved solids) occurs in strata closer to the surface, with slightly saline water (1,000 mg/13,000 mg/l total dissolved solids) in deeper aquifers.

Groundwater contamination is particularly bad because it is longlasting, difficult to trace, and may be very far-reaching. Once a layer of permeable sand has been polluted, it may be years before dilution and percolation clear the contaminant away. Though the actual rate of flow varies among aquifers, 200 feet per year has been suggested as a reasonable rate.[1] At this rate of flow, 260 years would be needed to clear an aquifer 10 miles from a river. Some aquifers flow as slowly as 20 feet per year, and would, therefore, require even longer to cleanse naturally. In the absence of a study detailing local subsurface hydrology, it is difficult to determine the source of a pollutant when one is found, or conversely to be certain that what is placed below the surface today will not one day contaminate a water supply.

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[1] A. Gene Collins, *Chemical Applications in Oil- and Gas-Well Drilling and Completion Operations*, U.S. Bureau of Mines, Bartlesville Petroleum Research Center, U.S. Department of the Interior, Bartlesville, Oklahoma, 1975.

Other mechanisms may play a part in mitigating or augmenting the impact of a discharge to an aquifer. These mechanisms are discussed in detail elsewhere in the report and are restated here in order to assess fully the incidence of pollution which may occur from tertiary oil recovery. It has been pointed out that the importance of each mechanism will vary with the hydrology and geology and other characteristics of the oil recovery project site. These mechanisms include: leading, dilution, adsorption, partitioning, chemical degradation, bacterial degradation, entrapment and precipitation. Figure 5-1 illustrates the role of these mechanisms in the fate of chemical leakage or spills resulting from tertiary oil recovery. The flow sheet is a general presentation of the order in which the mechanisms may act (if at all) on a chemical constituent in a leak. In fact, each mechanism may act upon the material a number of times.

5.1.2 Sources of Pollutants

The most serious problems arise when produced water or brine enters the groundwater system. Pollution may result from a variety of sources. If the brine is used to displace oil in a foreign formation, as in waterflooding, the brine may mix with nearby water supplies. Excess brine disposed into foreign strata may cause contamination of surrounding aquifers. Spills at the well head and seepage from pits may ultimately reach groundwater sources. Reinjecting brine into its original stratum is a common and usually safe method of disposal, but it, too, may allow contamination if the disposal well fails.

5.1.3 Mechanisms of Pollution

Three basic mechanisms of groundwater pollution have been distinguished: (1) bypassing the natural filtering system, (2) overwhelming the natural filtering system, and (3) altering the hydraulic or chemical balance of the system.[1]

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[1] U.S. Environmental Protection Agency, Ground Water Pollution from Subsurface Excavations, EPA-430/9-73-012, 1973.

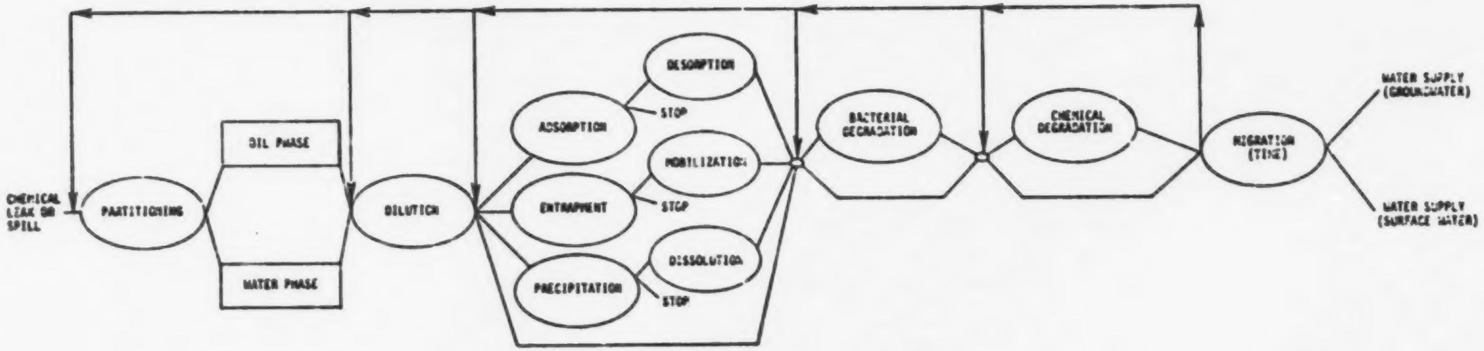
CHEMICAL LEAK OR SPILL
PARTITIONING
OIL PHASE
WATER PHASE
DILUTION
ADSORPTION
STOP
DESORPTION
ENTRAPMENT
STOP
MOBILIZATION
PRECIPITATION
STOP
DISSOLUTION
BACTERIAL DEGRADATION
CHEMICAL DEGRADATION
MIGRATION (TIME)
WATER SUPPLY (GROUNDWATER)
WATER SUPPLY (SURFACE WATER)

Figure 5-1. This figure shows that between the source of a spill or leak of chemicals used in tertiary oil recovery and a water supply there are a number of physical and chemical mechanisms which may act on the material.

5.1.3.1 Bypassing the Natural Filter

An opening in the formation -- such as an oil well -- may allow pollutants to pass directly into an aquifer without percolating through soil, rock, and organic matter. Bypass has posed and is likely to continue to pose most of the petroleum-related risks to groundwater supplies. Any break in the impermeable layers surrounding groundwater supplies lays open the possibility of pollution. Figure 5-2 shows the manner in which saline water may enter fresh water, polluted water may enter clean water, or substances from the surface may be washed into groundwater.

Though the bypassing of the natural filter may occur in a number of ways, the most common route is well failure. Any permeable stratum penetrated by a well is susceptible to contamination by oil, brine and chemicals passing through the well during both injection and extraction operations. Figure 5-3 shows a producing oil well and the possible routes of pollution into water-bearing strata. The newly-drilled wellbore is lined with metal pipe called casing which is cemented to the sides of the hole for rigidity and corrosion resistance. Surface casing is installed near the well head to keep the hole clear and to protect shallow fresh water aquifers. Production casing runs the length of the well. The bottom of the hole is plugged with a shoe, and a packer set inside the casing seals off the well just above the oil-bearing strata. Fluids pass through tubing which is suspended inside the casing and which passes through the packer. The result is a multiple shield between groundwater supplies and oil field fluids.

Yet ruptures do occur. The well provides communication among strata by conducting fluid through the cement-formation annulus, through the casing-cement annulus and then through a crack in the cement, through the tubing-casing annulus and then through cracks in the casing in the cement, or through the tubing and then through holes in tubing, casing, and cement.

5.1.3.2 Overwhelming the Natural Filter

The natural filtering system is overwhelmed when the contaminants become so concentrated that percolation cannot render the solution harmless. Seepage from brine pits pollutes in this manner (Figure 5-4). Recently, most states

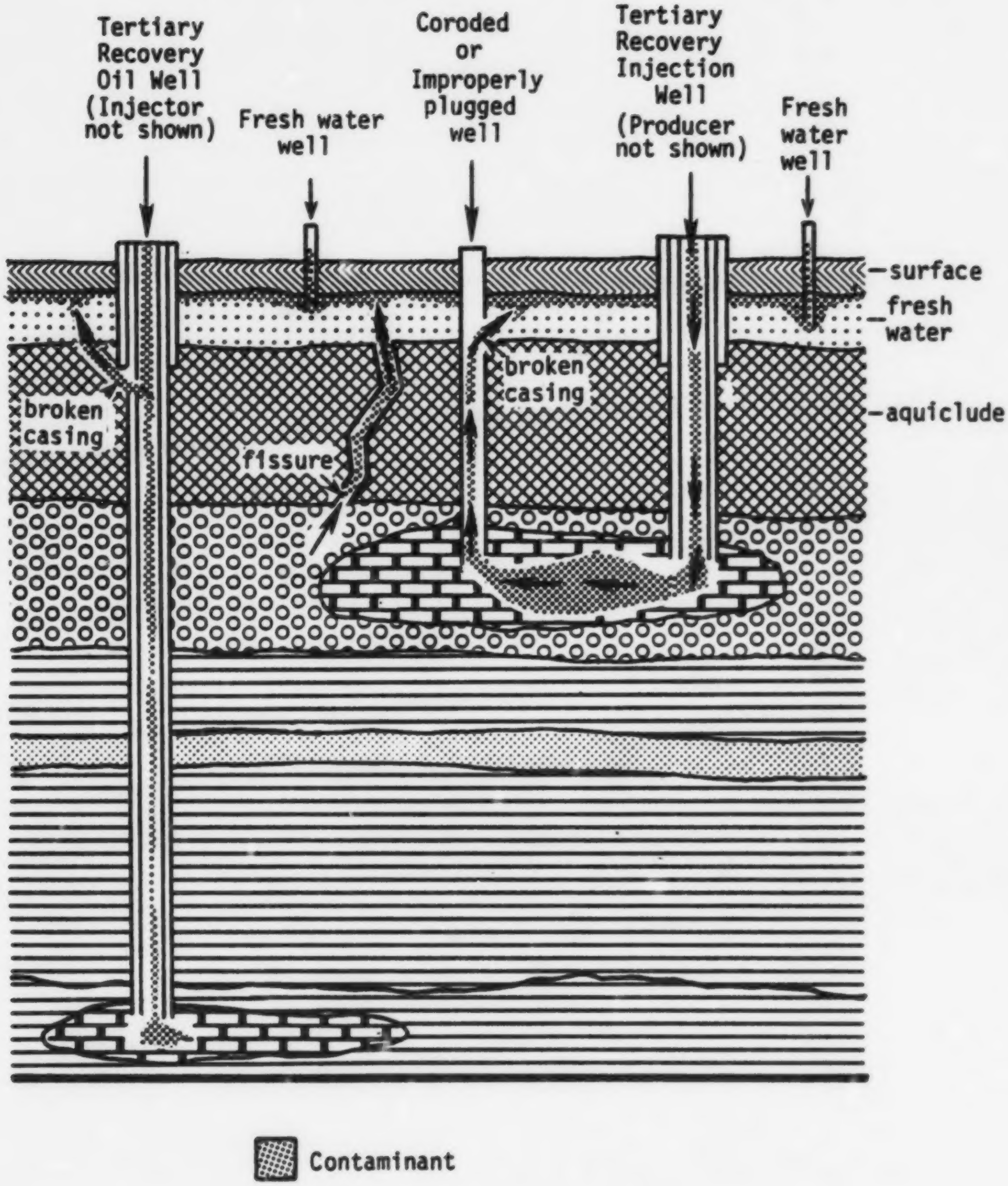
Tertiary Recovery Oil Well (Injector not shown)
Fresh water well
Coroded or Improperly plugged well
Tertiary Recovery Injection Well (Producer not shown)
Fresh water well
surface
fresh water
aquiclude
broken casing
broken casing
fissure
▩ Contaminant

Figure 5-2. This figure illustrates the contamination of fresh water through by-pass of the natural filter system.

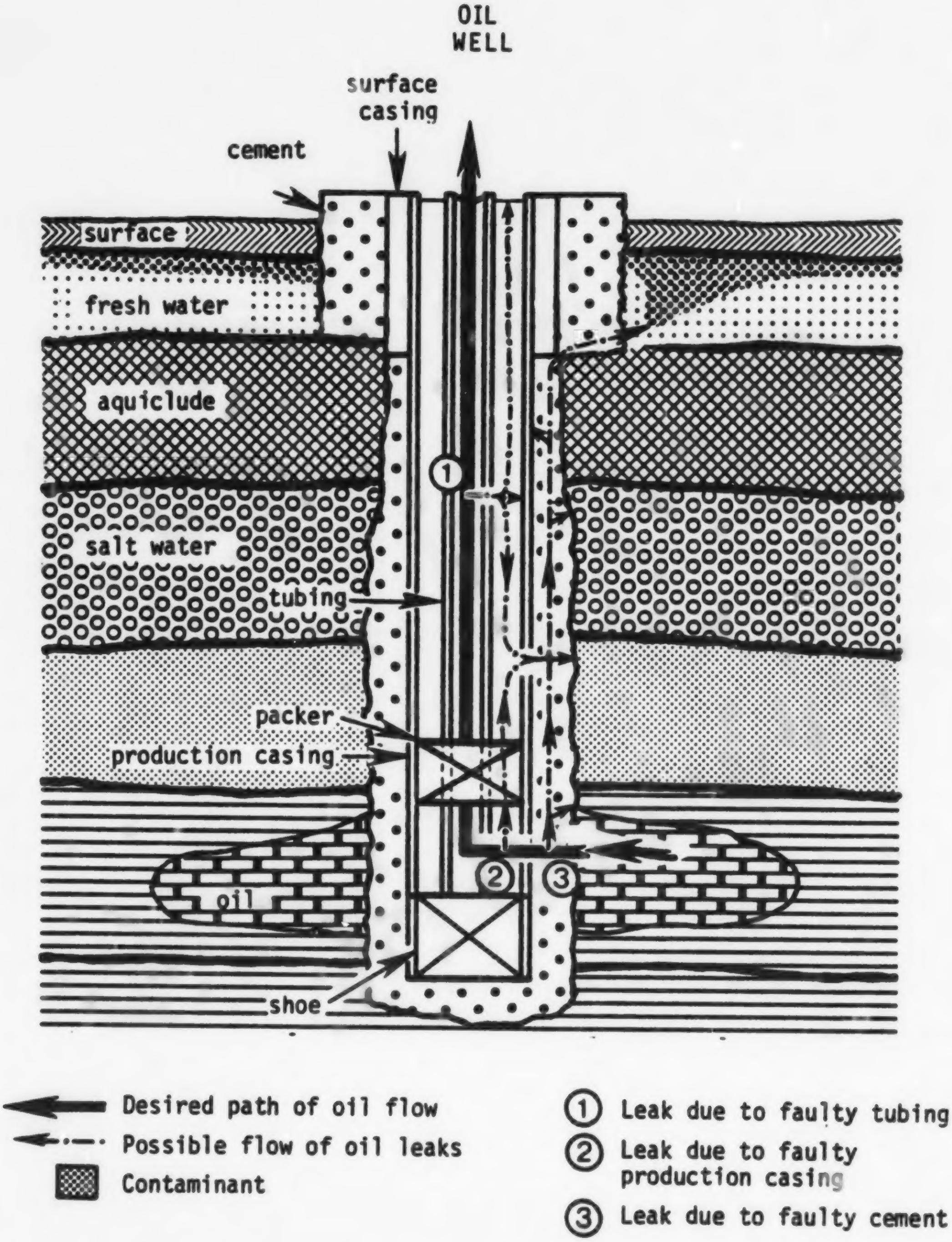
OIL
WELL
surface
casing
cement
surface
fresh water
aquiclude
①
salt water
tubing
packer
production casing
oil
②
③
shoe
Desired path of oil flow
Possible flow of oil leaks
Contaminant
① Leak due to faulty tubing
② Leak due to faulty production casing
③ Leak due to faulty cement

Figure 5-3. This figure is a diagram of an oil well showing the potential paths of fresh water contamination resulting from well failure.

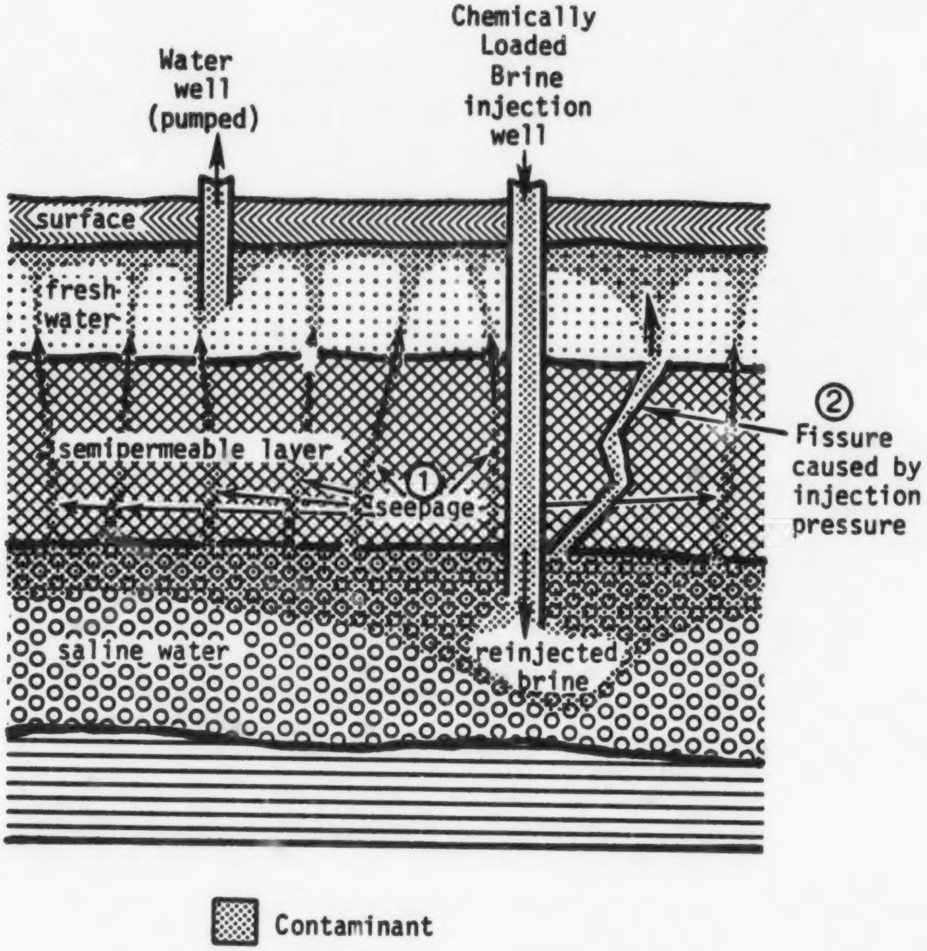
Water well (pumped)
Chemically Loaded Brine injection well
surface
fresh water
semipermeable layer
① seepage
② Fissure caused by injection pressure
saline water
reinjected brine
Contaminant

Figure 5-4. This figure illustrates the contamination of fresh water by chemically loaded brine through (1) overwhelm of natural filter system, and (2) pressure.

have recognized this danger and required that all disposal pits be impervious. The result has been a dramatic reduction in the amount of new pollution from this source. Of the complaints concerning brine seepage in Texas Railroad Commission District III since this law went into effect in 1973, most have been traced to continuing seepage from earlier disposal. The difficulty with brine seeps and chemical spills, as with groundwater pollution in general, is their longevity. The risk of chemical spills and seeps is difficult to quantify because many site-specific factors such as operator skill, systems design and construction, modes of shipment, and weather, will interact at each location. Spills which do occur may have longlasting effects on groundwater.

5.1.3.3 Changing the Formation

Differences in pressure, temperature, or chemical concentration cause the flow of groundwater; changes in temperature and acidity alter the sorptive properties of the formation. Within aquifers or inter-aquifer channels (wells or fissures) water flows from higher to lower pressure zones; to a lesser extent, flows are affected by concentration and temperature differentials. This can result in movement of saltwater into freshwater zones in the same aquifer, into other aquifers containing fresh water, or into surface water (Figure 5-5). If the formation has held toxic substances from another source, a disruption of the chemical balance may cause the release of such substances into groundwater.

5.2 Estimates of Probability of Contamination

The probability that chemicals will escape after tertiary recovery can be assessed roughly by reviewing the record of contamination under primary and secondary processes. The record chosen for examination is that of Texas Railroad Commission District III. This area contains numerous fields which are likely sites for each of the four tertiary recovery methods. The district has no peculiar features which might affect the incidence of problems: the formation fluids are not very corrosive and the risk of earthquakes within the area is very low. District III oil fields produce 5 percent of U.S. oil or roughly 60 million barrels per year.

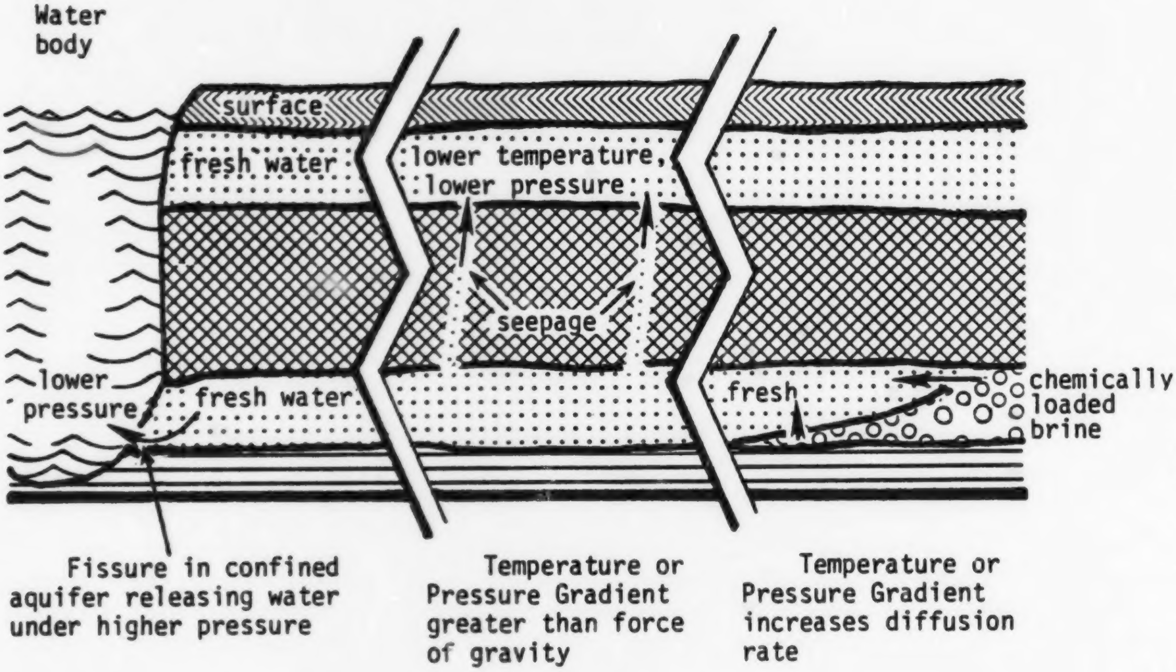
Water body
surface
fresh water
lower temperature, lower pressure
seepage
lower pressure
fresh water
fresh
chemically loaded brine
Fissure in confined aquifer releasing water under higher pressure
Temperature or Pressure Gradient greater than force of gravity
Temperature or Pressure Gradient increases diffusion rate

Figure 5- 5. This figure shows the manner in which differences in pressure, temperature and chemical concentrations affect the flows of water in aquifers.

Its major oil fields produce from some 8,000 wells. Even with this amount of production, the sample of problems is too small to arrive at a precise number for the probability of contamination, but it is possible to estimate the order of magnitude of the risk.

A conservative estimate of the probability of contamination can be obtained from the frequency of recorded incidents of a kind which could recur. The complaints of water pollution from oil-producing activities filed with the Railroad Commission over the past five years are summarized in Table 5-1A, broken down by source of pollution and type of water. Due to a change in the law as of 1973, many past causes of water pollution are no longer a problem. Since 1973, brine disposal in Texas has been permitted only into impervious subsurface pits. Therefore, the past incidence of pollution from surface discharge or unlined brine pits is no reliable guide to future probabilities of pollution. The past frequency of pollution through well failures is indicative of the expected scope of the problem.

Table 5-1B shows the number of incidents of water contamination which have occurred in spite of the new regulations, a measure of the future risks. Seven complaints of groundwater pollution from well failure were filed with the Texas Railroad Commission during 1973, 1974, and the first half of 1975. Surface pollution has been registered eight times in the same period. Since 1970 there have been over 90 on-lease oil spills at production, transportation, and storage sites.

The Chiquot aquifer, for example, flows at a rate of only 40 feet per year. Consequently, the time required for contaminants to appear is long and the wells from which the leakage occurs may take years to be pinpointed as offenders.

An estimate of the actual magnitude of the groundwater pollution problem can be obtained by determining what fraction of oil wells and disposal pits are so situated that pollution from the well site would reach a water well within five years. This can be calculated from a knowledge of groundwater hydrology, and of well locations in the area. The latter information is available from the Texas Water Development Board. If it is estimated that 40 percent of oil wells and pits are on groundwater flow routes that would reach a water supply within five years, and groundwater

TABLE 5-1A

TERTIARY OIL RECOVERY

TABULATION OF CONTAMINATION INCIDENTS REPORTED IN TEXAS RAILROAD COMMISSION DISTRICT III, 1970-75

ALL INCIDENTS[a]

CONTAMINANT	SPILLS	SEEPS		WELL LEAKS		DIRECT DISCHARGE
	TO SURFACE	TO SURFACE	TO GROUND-WATER	TO SURFACE	TO GROUND-WATER	TO SURFACE
BRINE	4	5	7	2	1	4
OIL	1	2	-	2	1	-
GAS	-	1	-	-	4	-
TOTAL	5	8	7	4	6	4

[a] In addition, three incidents of contamination were of undetermined causes. They were: 1) surface-oil; 2) surface-oil and brine; 3) groundwater-brine. One cause was determined as a seep of brine, but the type of water affected was not reported.

TABLE 5-1B

TERTIARY OIL RECOVERY

CONTAMINATION COMPLAINTS[a] SINCE REQUIREMENTS OF IMPERVIOUS BRINE DISPOSAL PITS, TEXAS RAILROAD COMMISSION DISTRICT III, 1970-75

CONTAMINANT	GROUNDWATER	SURFACE WATER
BRINE	3	6
OIL	-	1
GAS	4	1
TOTAL	7	8

[a] These incidents are representative of risks from tertiary processes, i.e., incidents of a type likely to recur, and which will cause new hazards with tertiary methods.

contaminants originating at an oil well or brine pit have been recorded ten times over five years, then the estimated incidence rate for District III is:

$$10 \text{ violations} \div 5 \text{ years} \div 0.4 \text{ sample} = \frac{5 \text{ violations}}{\text{year}} \tag{5-1}$$

This gives the order of magnitude of the contamination rate. A longer counting period would probably give more reliable results, but good records are only available since 1970. The failure rate of wells in District III, in fields under tertiary recovery is:

$$\frac{5 \text{ violations}}{\text{year}} \div 8{,}000 \text{ wells} = 0.006 \frac{\text{violations}}{\text{year}} \tag{5-2}$$

On a national scale this well failure rate suggests that approximately 175 wells in fields involved in tertiary recovery projects might fail each year and release reservoir fluids into water supplies.

Another estimate of the probability of contamination from an oil well can be obtained from data on the frequency of well failure and an understanding of how failures may result in contamination. Statistics for well failures requiring repairs in 1974 are included in Table 5-2. The "other" category covers all nonmechanical failures in operating wells, such as well-bore leaks and poor cement jobs. The incidence of "other" repairs on Table 5-2 probably overstates the likelihood of well leakage because mechanical problems such as plugged lines, sanding up, etc. which are included in the category will not necessarily result in pollution. However, in order to obtain a first-order estimate of what is perhaps the upper bound of failure risk, it will be assumed that this figure primarily registers failures which resulted in communication between the well system and other formations.

From an environmental standpoint, failures of plugged and abandoned wells are of greater concern than failures of operating wells because there are no monitors of these leaks. Operating wells do fail as shown in Table 5-2, but economic incentives and environmental controls on the well operator should minimize the amount of leakage which occurs. Leakage from an injection well may reduce the effectiveness of tertiary recovery or result in the needless loss of expensive chemicals. Production well leaks may result in loss of oil or higher than necessary pumping expense to lift the additional water which infiltrates the well.

TABLE 5-2

UNITED STATES WELL FAILURES - 1974
(Failure Divided By Total Wells Involved)

TYPE FAILURE	WEST COAST	MID-CONTINENT	PERMIAN BASIN	ROCKY MOUNTAINS	EAST TEXAS	TEXAS GULF COAST	SOUTHEAST U.S.
SUCKER RODS	0.31	0.48	0.52	0.31	0.12	0.56	0.15
ROD PUMPS	0.58	0.51	0.52	0.44	0.20	0.35	0.54
TUBING STRINGS	0.22	0.17	0.14	0.12	0.05	0.58	0.05
OTHERS[a]	0.03	0.34	0.28	0.22	0.18	0.09	0.20
AVERAGE FAILURE INCIDENCE	1.08	0.82	1.00	0.77	0.25	0.61	0.56

[a] Average "OTHER" failure incidence was 0.18 on a nationwide basis.

SOURCE: J.E. Kastrop, "Downhole Oil Well Maintenance Costs Push Half Billion", Petroleum Engineer, (July 1975): 22.

Furthermore, the probability of failure in the production wells or abandoned wells within a producing field may be conceptualized as proportional to the depth (or distance) between the oil reservoir and the nearest aquifer uphole. In general, fluid level in the producing well is kept at less than 500 feet above bottomhole (or pressures about 200 pounds per square inch gauge at bottomhole) though pump capacity limitations may result in fluid levels up to approximately 1,000 feet above bottomhole. Therefore, aquifers separated by more than 1,000 feet of sediments from the oil reservoir would be very unlikely to be exposed to reservoir fluids.

The abandoned field leakage problem is more complex. Geologic changes or incursion of water or fluids from another source may force reservoir fluids through leaks in the well which developed over time after tertiary recovery has been complete. Many intraregional factors will affect the actual incidence rate. The operating well data on Table 5-2 are indicative of these factors, which it is assumed, will act in a similar way in the abandoned well. As a "worst case" analysis of this problem, leakage from abandoned wells will be related to the proportional thickness of aquifers penetrated by the well to total well depth. If the corrosiveness, well ages and other factors are assumed to be uniform throughout a region,[1] then a well four-thirds as deep as the average for the area can be expected to have a failure rate four-thirds as high as that listed in Table 5-2. The incidence of contamination (P_c) within a field in terms of incidents per well-year is then:

$$P_c = \text{Regional Incidence} \times \frac{\text{Field Depth}}{\text{Regional Average Well Depth}} \tag{5-3}$$

$$\times \frac{\text{Aquifer Thickness}}{\text{Field Depth}}$$

$$= \text{Regional Incidence} \times \frac{\text{Aquifer Thickness}}{\text{Regional Average Well Depth}} \tag{5-4}$$

---

[1] Operators have noted that, in fact, corrosion is highly localized and related to the aquifer itself. Furthermore, casing coatings, though more expensive than cathodic protection systems used during the operating life of the well, are sometimes employed.

The expected incidence of groundwater contamination through well failure is the product of the expected failure incidence and the probability of contamination given that the well leaks. Disregarding differences in the corrosiveness of geologic strata, the chances of a leak at any point throughout the well's depth are equal. When a break occurs, in an abandoned well the probability that an aquifer will be polluted is roughly the fraction of the well length which penetrates water-bearing strata.

The following example illustrates this estimation procedure. Figure 5-6 depicts the Conroe field in Montgomery County, Texas, with 727 wells and a reservoir depth of 5,200 feet. A survey of well data at the Texas Railroad Commission shows that the average well depth in District III is 5,000 feet. Table 5-2 indicates an average failure incidence of 0.09 for the area. Fresh water is found in the Evangeline and Upper Jasper aquifers. Out of 5,200 feet of oil well, 1,400 feet penetrate fresh water. The primary water supply is the Evangeline aquifer, which intersects the upper 1,000 feet of the wells. Slightly saline to saline water is found in the lower part of the Jasper aquifer, and in 600 feet of the section below 4,000 and above 6,000 feet. This makes the total thickness of all water-bearing sands 4,000 feet for a 5,200 foot well. Table 5-3 shows the estimated contamination incidence for Conroe, and the implication for all of District III, assuming these sections are representative. Equation 4 indicates that contamination incidence depends only on the thickness of aquifers. Thermal methods show a lower rate because the processes are limited to shallow sands down to 3,000 feet. The estimated number of incidences of groundwater contamination is calculated for each process by multiplying the number of wells projected to be involved by the incidence rates. This does not account for the phased development of these projects over time. For example, if micellar-polymer projects were conducted over a 20-year period, about three incidents of freshwater supply contamination would be expected.

It is not possible to project this failure incidence to other regions or to a national scale because data have not been developed on the depths of all wells and the total thickness of the aquifers penetrated. Considerable risk variation exists even among counties in the same district. Local differences result from both natural and historical characteristics. These aspects and the direct effect of the tertiary recovery processes on risk are evaluated in the following section.

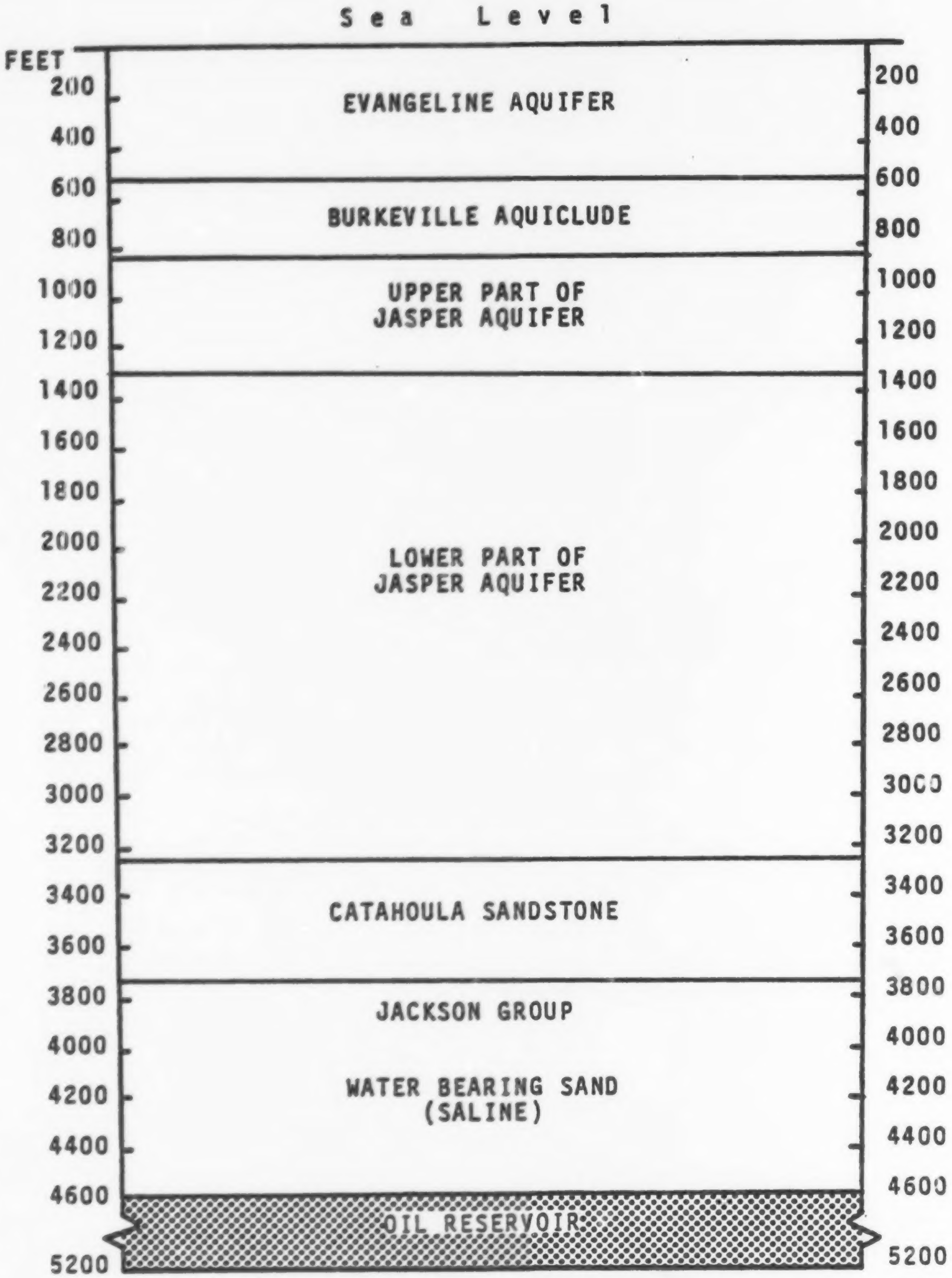
Sea Level
FEET
200
400
600
800
1000
1200
1400
1600
1800
2000
2200
2400
2600
2800
3000
3200
3400
3600
3800
4000
4200
4400
4600
5200
EVANGELINE AQUIFER
BURKEVILLE AQUICLUDE
UPPER PART OF JASPER AQUIFER
LOWER PART OF JASPER AQUIFER
CATAHOULA SANDSTONE
JACKSON GROUP
WATER BEARING SAND (SALINE)
OIL RESERVOIR

Figure 5-6. This figure illustrates a cross section of a typical well in the Conroe Field, Montgomery County, Texas (Railroad Commission, District III) showing the location and thicknesses of the important aquifers and their relationship to the oil bearing zone.

TABLE 5-3

TERTIARY OIL RECOVERY

EXPECTATION OF POLLUTION INCIDENTS IN DISTRICT III, TEXAS[a]

WATER QUALITY	DEPTH	INCIDENCE[b] (Contamination Incidents/well-year)	CONROE	MICELLAR	THERMAL	CO_2
	TYPICAL DEPTHS		5,200'	5,000' (max.)	3,000' (max.)	7,500
	NUMBER OF WELLS		727	3,491	1,622	2,182
Fresh supply	1,000'	.018	14	63	29	39
All fresh	1,400'	.025	19	88	41	55
Fresh to slightly saline	3,400'	.061	45	214		133
	(3,000' thermal)	(.054 thermal)			88	157
All water	4,000'		52	251		
	(3,000 thermal)	(.054 thermal)			--	--

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[a] Expected number of incidents = (number of wells) x incidence per year.

[b] Incidence calculated as (regional incidence) x $\frac{\text{thickness of water}}{\text{regional average well depth}}$

For example, micellar fields incidence of contamination of fresh water supplies = .09 x $\frac{1,000}{5,000}$ = .018. The annual number of incidents is .018 x 3,491 wells = 63 incidents in micellar fields at full development.

5.3 Analysis of Factors Affecting Risk

Risks of contamination of groundwater within a given oil field are affected by the tertiary oil recovery process chosen for the field, the ages of the wells drilled into or through the formation in which the tertiary recovery will be carried out, and the seismicity in the area.

Wells provide communication among strata by conducting fluid along various paths in the wellbore, as shown in Figure 5-2. Leaks can be caused by: (1) faulty casing connections, (2) corrosion, (3) inadequate casing seal at the shoe, (4) perforation at the wrong point, (5) fissures in cement or casing caused by high pressure, (6) poor cementing, and (7) earthquake damage.

Corrosion and pressure are the greatest problems. The tertiary recovery method which is selected may raise the risk of groundwater contamination by further increasing pressure or corrosion rate. Table 5-4 lists some of the typical operating conditions for recovery methods and compares these conditions with operations during primary and secondary recovery.

Increased pressure during injection of the tertiary recovery fluids into the reservoir are unlikely to fracture aquicludes or wellbore cement. As shown in Table 5-4, there is a margin of safety between the operating pressures used in tertiary recovery and a conservative estimate of the hydraulic fracture strength of the reservoir rock. The safety factor ratio is smallest for the steam injection reservoir and largest for carbon dioxide processes.

Brine disposal wells present problems for two reasons: first, they are frequently old wells, converted to disposal after a reservoir has been exhausted; secondly, pressure is often used to inject brine. The pressure can fracture aquicludes, allowing migration of brine into fresh water and aquifers. To avoid this, bottom-hole pressure should be less than one pound per square inch per foot of well depth.[1] Pressure-induced fractures are usually horizontal in formations as deep as 1,000 feet and are vertical below 1,500 feet.[2] Fractures in formations deeper than 1,500 feet might provide communication between strata.

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[1] A.G. Collins, "Oil and Gas Wells - Potential Polluters of the Environment," Journal of Water Pollution Control (December 1971): 2390.

[2] Collins, Oil and Gas Wells," p. 2391.

TABLE 5-4

TERTIARY OIL RECOVERY

MAXIMUM OPERATING CONDITIONS IN SOME TYPICAL PROCESSES

	TERTIARY RECOVERY METHOD			
	MICELLAR-POLYMER	STEAM	COMBUSTION	CARBON DIOXIDE
Assumptions: (Typical Project)				
Reservoir Permeability (millidarcies)	500	500	500	100
Spacing between Wells (feet)	1000	500	1000	2000
Well Depth (feet)	5000	3000	5000	8000
Initial Pressure (lb./in.^{2})	2500	1500	2500	4000
Maximum Pressure during Secondary Recovery[a,b] (lb./in.^{2})	3500	1500	3000	4000[b]
Maximum Pressure during Tertiary Recovery[b] (lb./in.^{2})	3500	2500	4500	4000
Maximum Temperature during Tertiary Recovery (°F)	150	600	1200	200
Hydraulic Fracture Strength of Reservoir Rock[c] (lb./in.^{2})	5000+	3000+	5000+	8000+
Pressure Safety Factor: $\left(\frac{\text{Hydraulic Strength}}{\text{Tertiary Recovery}}\right)$	1.4:1	1.2:1	1.2:1	2:1
pH of Residual Fluids	6-8	6-8	2-4	4
Conductivity of Residual Fluids	Moderate	Moderate	High	High

[a] Non-miscible gas injection or waterflooding.

[b] At injector wells bottomhole.

[c] Minimum value for reservoirs.

Some early steam injection projects "blew out," damaging the formation and overburden or fracturing the cement and rupturing or buckling the casings in injection wells. The surface fittings broke on a carbon dioxide sulfide injection well in Texas resulting in several deaths by H_2S poisoning. The latter accident was caused by a part which failed at an operating pressure below the 10,000 pounds per square inch for which it had been rated.

Though some pressure failures have occurred in the past, they are very unlikely during tertiary recovery operations. There is a margin of safety in the operating pressures of the project and pressures will rarely exceed the original pressure of the fluids confined in the oil-bearing strata. A high pressure is required to initiate in-situ combustion, but it is only of brief duration. Average operating pressures in a fireflood are 500 to 600 pounds per square inch.

Generally, chances of well failure from applying too much pressure to the reservoir during tertiary recovery are exploratory drilling. Drilling in a new geologic province such as the Outer Continental Shelf, there is little knowledge of the geopressures that will be encountered. When tertiary recovery is begun, a great deal of information is available about the oil field. These data provide the basis for sound engineering decisions in the design and operation of tertiary oil recovery projects. The large front-end investment required in tertiary recovery is an additional incentive for monitoring and controlling operating pressures of the project. In a micellar-polymer flood, the expensive chemicals in the slug could be lost to a fracture before any additional oil had been recovered. Similar considerations should raise operator awareness of chemical spills at the surface during formulation and injection. The operator of a carbon dioxide project or in-situ combustion project must pay for every additional pound per square inch of injection pressure used. Steam injection methods, applied at shallow reservoir depths, still require caution to avoid fracturing the overburden rocks. But problems with injection wells in steam injection have largely been solved by improved cements and completion methods, which compensate for the thermal expansion of the casing.

Corrosion is more of a problem with some tertiary recovery methods. The corrosion rate of steel well casing is affected by the pH and conductivity of the fluids which contact it. Temperature also influences the rate of corrosion. Considering the data on Table 5-4, the corrosiveness of the recovery methods can be evaluated. Table 5-5 ranks the relative corrosiveness of the tertiary recovery methods in relation to primary and secondary recovery. The ranking is based on the corrosiveness of the fluids which remain in the reservoir after the recovery project is completed and on the equilibrium temperature of the oil-bearing strata. Carbon dioxide processes and the thermal methods of tertiary oil recovery are relatively more corrosive than micellar-polymer flooding. The ranking is based upon the assumption that process is the only variable. The actual effect of these processes on corrosion of particular wells is dependent on the completion practices, materials used in construction, rock formations, and even the expertise of the operator. Specific data on these factors in each region or field are limited and an analysis of the interrelationships of these variables is beyond the scope of this assessment.

For an initial appraisal of these factors, a methodology based on the ages of the reservoirs and number of wells within the major oil fields where tertiary recovery is feasible was developed as discussed in Appendix A. Table 5-6 displays the estimated age profile of wells which may be involved in each tertiary recovery method within each region. For example, the table shows that 75 percent of all oil wells which may be involved in micellar-polymer flooding in the Pacific West Region are less than 35 years old. These wells were completed with modern materials and practices more oriented to safety and conservation. Generally, wells or reservoirs that are older were completed in a less sophisticated manner. The divisions of age into three groupings mark distinct changes in the state-of-the-art of oil well drilling, completion and production, as well as differences in the economic and regulatory climate affecting the petroleum extraction industry.

It is not particularly surprising to note the skew toward older ages in the age profile of thermal wells in each region. Many of the shallow, low-gravity oil fields were originally discovered by surface evidence and natural seeps. Although most producing wells in these fields may not date from the turn of the century since they can be redrilled relatively cheaply, using the age profile as a risk indicator is valid since failure of the old plugged and abandoned wells is still possible.

TABLE 5-5

TERTIARY OIL RECOVERY

RELATIVE CORROSIVENESS OF RECOVERY METHODS

Most Corrosive:	Carbon Dioxide Miscible
	In-situ Combustion
	Steam Injection
	Secondary Recovery Waterflood[a]
Least Corrosive:	Micellar-Polymer Flooding
	Primary Recovery[b]

[a] Assumes that a higher conductivity brine is used for the waterflood. Actual corrosiveness will be affected by local geochemical conditions within the oil reservoir and penetrated formations.

[b] Assumes that the brine from the oil-bearing strata is of lower conductivity than water used in waterflooding. This is generally true for shallower reservoirs where thermal methods and micellar-polymer floods are feasible. Actual corrosiveness will be affected by local geochemical conditions encountered such as salt sections, high partial pressure of naturally-occurring carbon dioxide in gas-condensate produced, or the presence of hydrogen sulfide.

TABLE 5-6

TERTIARY OIL RECOVERY

FRACTION AND NUMBER OF WELLS IN MAJOR OIL FIELDS OF EACH REGION WHERE TERTIARY RECOVERY IS FEASIBLE

TERTIARY RECOVERY METHOD	DATE OF WELLS	PACIFIC	ROCKIES	NORTH CENTRAL	SOUTH CENTRAL	SOUTH EAST	NORTH EAST	TOTAL
Micellar	≤1920	20% (512)	83% (1,656)	21% (2,580)	10% (1,421)	56% (247)	NA	18% (6,416)
	1921-1940	5% (117)	17% (350)	63% (7,788)	88% (12,222)	71% (3,334)	NA	67% (23,811)
	≥1941	75% (1,893)	NA	16% (1,920)	2% (258)	24% (1,150)	NA	15% (5,221)
Thermal	≤1920	76% (21,820)	100% (701)	NA	21% (1,622)	94% (8,533)	NA	68% (32,676)
	1921-1946	20% (5,593)	NA	100% (1,920)	79% (6,090)	2% (166)	NA	29% (13,769)
	≥1941	4% (1,138)	NA	NA	NA	4% (383)	NA	3% (1,521)
Carbon Dioxide	≤1920	20% (129)	21% (540)	NA	42% (11,772)	62% (8,886)	NA	42% (20,727)
	1921-1940	14% (90)	79% (1,995)	98% (5,227)	34% (9,461)	31% (4,067)	NA	42% (20,840)
	≥1941	66% (414)	NA	16% (53)	24% (6,579)	7% (912)	NA	16% (7,958)

NA: None or data not available.

Abandoned wells which have been inadequately plugged are frequent sources of contamination at present. Once production wells have ceased operation and have been plugged, no one is concerned with keeping them in good condition. Even when leaks are detected, sometimes no one can be held responsible. The Texas Railroad Commission has about $100,000 allotted annually for replugging operations, but this sum is hardly sufficient since it costs approximately $10,000 to find and plug a single abandoned well. The problem of leakage of old wells has hindered enhanced recovery operations in parts of New York and Pennsylvania. Wells dating from the late 1880's, were often crudely plugged with tree saplings if they failed to reward the early "wildcatter" sufficiently. Today, leakage from these old-time wells can jeopardize the success of any tertiary recovery project which is otherwise potentially viable.

Most wells need casing repairs by the time they are 10 to 14 years old. In the Texas Upper Gulf Coast, for example, such repairs were required at a rate of 0.09 repairs per well per year, or about 11 years mean time between well failures.[1] Older wells are more likely to leak, both because of general aging and corrosion and because earlier technologies of materials, completion, corrosion protection, and plugging were less reliable.

5.4 Relative Regional Risk Levels

An analysis of the age profile of wells involved in tertiary recovery yields a ranking of the relative risks of well failure in each region. Tables 5-7, 5-8 and 5-9 present the rankings. A number of factors which are complex and interrelated have been excluded from the rankings for this investigation. Local geochemical conditions may affect well failure rates. Failure incidence is also a function of the depth of the wells involved in each recovery method in each region. The well spacing and number of wells within an oil field also affect the risks presented by each project. But the data have not been developed on these variables.

Seismic activity can also cause damage to wells in a tertiary recovery project, allowing reservoir fluids to migrate into aquifers. Figure 5-7 is a seismic risk map of

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[1] J.E. Kastrop, "Downhole Oil Well Maintenance Costs Push Half Billion," Petroleum Engineer (July 1975): 22.

TABLE 5-7

TERTIARY OIL RECOVERY

RELATIVE REGIONAL RISK OF WELL FAILURE FOR MICELLAR-POLYMER FLOODING[a]

(Excludes seismic risk and local variations in geochemical corrosiveness)

Most likely to fail:	Rocky Mountain
	South Central
	North Central
	South East
Least likely to fail:	Pacific West

---

[a] Northeast Region not ranked due to lack of data but is probably at a comparable risk level with the Rocky Mountain Region.

TABLE 5-8

TERTIARY OIL RECOVERY

RELATIVE REGIONAL RISK OF WELL FAILURE FOR CARBON DIOXIDE MISCIBLE METHODS[a]

(Excludes seismic risk and local variations in geochemical corrosiveness)

Most likely to fail:	Southeast
	South Central
	Rocky Mountain
	North Central
Least likely to fail:	Pacific West

---

[a] Northeast Region not ranked due to lack of data, but risk level is probably comparable to the South Central Region.

TABLE 5-9

TERTIARY OIL RECOVERY

RELATIVE REGIONAL RISK OF WELL FAILURE FOR THERMAL METHODS OF OIL RECOVERY[a]

(Excludes seismic risk and local
variations in geochemical corrosiveness)

Most likely to fail:	Pacific West
	Southeast
	South Central
Least likely to fail:	North Central

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[a] Northeast and Rocky Mountain Regions not ranked due to lack of data. Risks of well failure in the Northeast and Rocky Mountains are probably comparable to the Pacific West and Southeast Regions, respectively.

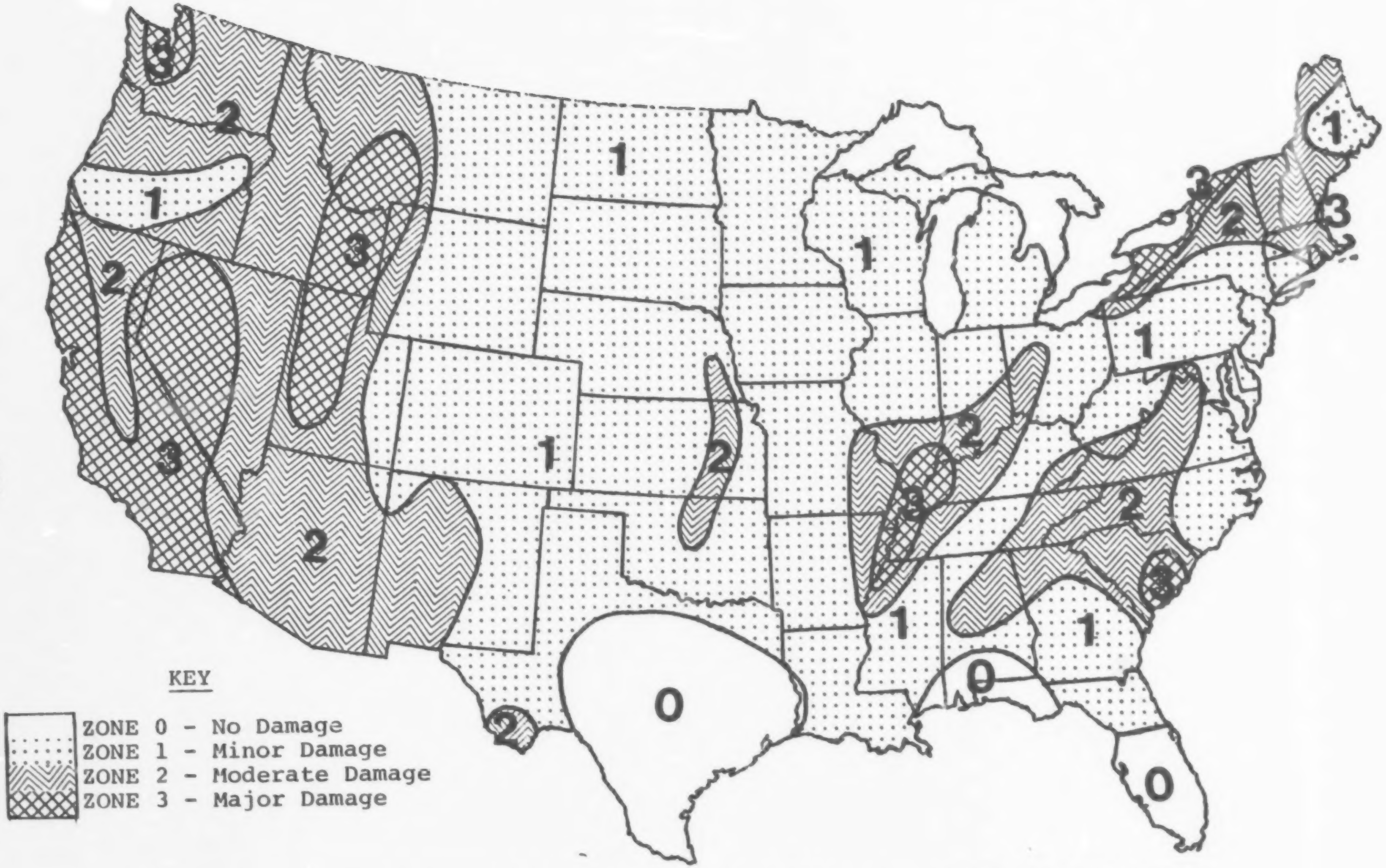
KEY
ZONE 0 - No Damage
ZONE 1 - Minor Damage
ZONE 2 - Moderate Damage
ZONE 3 - Major Damage
0
1
2
3

Figure 5-7. This figure is a seismic probability map of the United States.

the United States. Earthquakes are virtually unknown in District III, and throughout most of Texas. But in some areas (e.g., Southern California) this risk is high and tremors may contribute to a high localized well failure rate. If localized well failure incidence is known, earthquakes may have contributed their share to that rate, and need not be considered as a separate factor. Note that the data of Table 5-2, however, give only an aggregate incidence for the West Coast. The location of the oil fields and the expected damage inflicted by an earthquake in each region was examined. The relative regional risk of well damage due to seismic activity is shown in Table 5-10.

TABLE 5-10

TERTIARY OIL RECOVERY

RELATIVE REGIONAL RISK OF WELL DAMAGE DUE TO SEISMIC ACTIVITY

(Excludes improvements in well completion technology to mitigate earthquate damage)

Most Severe Damage:	Pacific West
	North Central
	Rocky Mountain
	Northeast
Minor Damage or No Damage:	Southeast
	Southcentral

CHAPTER SIX

IMPACT OF TERTIARY OIL RECOVERY ON AMBIENT AIR QUALITY

6.0 Introduction

Thermal methods of enhanced oil recovery could add as much as 10 billion barrels to the Nation's recoverable reserves as discussed in Chapter Three. In-situ combustion techniques are still undergoing field testing and are in an early stage of development, but steam displacement projects are being expanded on a commercial scale. The Energy Research and Development Administration forecasts that nearly one-half of the oil recovered by advanced techniques through 1985 will be produced by steam injection. Since steam displacement will play a major role in near-term enhanced recovery activity, dispersion modeling of two "typical" sizes of projects was carried out to evaluate their air quality impacts.

In-situ combustion projects were not modeled because of the following factors: (1) Uncontrolled emissions from producing wells are released at ground level and would have little, if any, vertical momentum vector. This would cause the highest concentrations of pollutants to occur within the oil field. (2) Chapter Two hypothesized the emissions of SO_x, NO_x and hydrocarbons would be small on the average and these expectations were supported by operator observations. These emissions may fluctuate over the duration of the "burn" as operating conditions vary. With small discharge quantities varying over time in a manner that is not fully understood, little would be gained by carrying out extensive dispersion modeling of these emissions. (3) A number of the fireflood operations indicated that vapor recovery systems to handle effluent gas and condense light hydrocarbon fractions for sale had proven to be economically justified. Though the scale economics of large vapor recovery systems may be less favorable in fieldwide firefloods due to the need for extensive gas gathering piping systems, there seemed to be little value in simulating a situation that is less likely to occur given the current practices in in-situ combustion projects.

6.1 Summary

Two hypothetical cases, a large project and a small project, were examined in three regions of the country in which the largest resource potential amenable to thermal oil recovery exists. These regions are: (1) the Central Valley of California, (2) the Northern Rocky Mountains, and (3) the Gulf Coast. Projects of two sizes were selected to encompass the range of projects which might be expected. These projects are defined below. In each case, moderate values of the operating conditions and meteorology were assumed, so that the predicted air quality impact would not be overstated by the computer-based dispersion modeling. The following conclusions regarding impacts on National Ambient Air Quality Standards are based upon an analysis of the cases and are very much dependent upon the assumptions used and the limits of the analysis which are discussed fully in Section 6.5:

1. The "typical" small steam displacement project in which steam generators burn approximately 1.23 percent sulfur fuel can be developed without violating National Ambient Air Quality Standards.
2. The "typical" large steam displacement project in which the steam generators burn about 1 percent sulfur fuel will violate the standard for SO_2. Crude oils in California oil fields which may undergo thermal oil recovery average approximately 2.1 percent. Combustion of these fuels would result in a situation worse than that represented here.
3. Existing fuel-burning rules in State Implementation Plans covering parts of California and all of Utah and Oklahoma are insufficient to insure attainment of NAAQS for regions in which full scale development of large oil fields by steam displacement may occur.
4. In order for a fully developed "typical" large project to comply with standards for SO_2, emissions from steam generation would have to be reduced to a level equivalent to burning approximately 0.57 percent sulfur fuel in current designed units.
5. NO_x emissions from the "typical" large projects will not exceed standards.

6. Only trace amounts of hydrocarbons and CO emissions from steam generators are expected because of the large amount of excess air used for combustion. A larger source of hydrocarbons may be the fugitive emissions of steam released at the producing wells. Control technologies for these emissions are within the state-of-the-art. This source and other possible point and area sources of hydrocarbons from enhanced recovery have not been characterized.

7. A number of control technologies and strategies are available to mitigate air quality impacts. An analysis of the impact of these strategies on regional air quality and the amount of oil which can be economically recovered is necessary for the development of sound environmental policy.

6.2 Methodology and Rationale

6.2.1 Description of Cases Modeled

Hypothetical steam displacement projects of two sizes were developed for the analysis. These two cases were selected to depict "typical" operations in the areas where thermal recovery is most likely to be carried out. Table 6-1 summarizes the assumptions and configurations for the "typical" projects. The hypothetical cases are based upon actual oil reservoirs and forecasted development patterns. However, the examples of existing projects are cited herein to point out the technical validity and conservatism of the assumptions. The results illustrate the magnitude of air quality problems which may occur as a result of large-scale thermal oil recovery and are not necessarily indicative of air quality in the vicinity of the ongoing projects which are mentioned.

For this analysis, the air quality impacts and levels of control required to meet standards were determined by examining the ambient air quality at and beyond the boundary of the oil field. Concentrations of pollutants were two to three times higher within the fields than outside the field boundaries. The basis for excluding the oil field in determining the maximum ambient air concentrations is that the oil field may be considered an industrial site in most nonurban

TABLE 6-1

THERMAL OIL RECOVERY "TYPICAL" OIL FIELDS

RESERVOIR DATA	PROJECT SIZE	
	LARGE	SMALL
Area (acres)	5,760	200
Depth (feet)	1,000	1,500
Thickness (net) (feet)	100	75
Porosity	20%	25%
Permeability (Millidarcies)	1,000	500
Oil Gravity (Degree API)	12	14
Oil Saturation (Barrels per Acre Foot)	1,500	1,800
Steam Displacement Data		
Oil Production (Gross):Fuel Ratio[a]	3.5:1	2.95:1
Installed Capacity (Million Btu/hr)	4,320	100
Recovery (% OIP)	40%	50%
Configuration 20 MM Btu/hr units	36	--
50 MM Btu/hr units	72	2

[a] Discussed in text Sections 6.2.1.1 and 6.2.2.2.

areas. These sites may be covered by OSHA regulation. Tighter controls would be required to comply with NAAQS within the boundaries of the large project. The "typical" fields were oriented so that the shortest distance between the generators and the boundary of the field is in the direction of the highest predicted SO_2 ground concentration.

6.2.1.1 Large Project Case

California has the largest oil resource base amenable to thermal oil recovery. Many of the oil reservoirs are either massive or multiple lenticular sand bodies which could result in a high density of steam generating units at full development. This large-scale development may also occur in Utah tar sands or in some older Gulf Coast area oil fields.

The size of the large project was chosen from an analysis of major oil fields in California corrected for skew in the size distribution attributable to very large fields (in excess of 13,000 acres). The data on the areal size of California fields are shown in Table 6-2. Average field size is 8,340 acres including the largest fields and 4,340 acres excluding all of the largest fields. Therefore, a typical field of 5,760 acres of nine sections (640 acres per section) was chosen with a 3-mile square (3 miles x 3 miles) configuration.

Steam generating capacity (for the large project) was estimated in the following manner. A reservoir with an oil saturation of 1,500 barrels per acre foot, a recovery efficiency of 40 percent and other characteristics shown on Table 6-1 requires steam input of 22,000 barrels of steam per acre-foot of oil reservoir at an assumed peak injectivity of 2,500 barrels steam per acre foot per year. This is the equivalent of 9,815 Btu/hr of capacity per acre foot of reservoir of 981,500 Btu's/hr of capacity per acre of oil field. By comparison, the oil fields near Bakersfield, California will have steam generator densities of 1,600,000 to 3,750,000 Btu/hr of capacity per acre of oil field at planned full development or nearly four times the density used in this study. Oil production is a net of two and one-half barrels for each barrel crude oil burned in the steam generators or a gross oil production to fuel ratio of 3.5:1.[1]

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[1] Personal communication with Getty Oil Company, Bakersfield, California.

TABLE 6-2

AREAL SIZE OF MAJOR CENTRAL VALLEY CALIFORNIA OIL FIELDS

FIELD SIZE GROUP	FIELD	SIZE (Acres)
Less than 3,000 acres	Rio Bravo	(2,000)
	McKittrick	(1,500)
	Greely	(2,100)
3,000 to 7,000 acres	Kern Front	(4,500)
	Mt. Poso	(3,500)
	Lost Hills	(3,900)
	Edison	(6,600)
	Fruitvale	(3,300)
	Coalinga Nose	(4,000)
	Coles Levee North	(3,800)
	Cymric	(3,300)
7,000 to 13,000 acres	Belridge	(9,200)
	Kern River	(8,700)
Over 13,000 acres	Coalinga	(19,300)
	Midway-Sunset	(24,900)
	Kettleman Dome	(13,700)
	Elk Hills	(19,600)
	Buena Vista	(16,300)

[a] U.S. Environmental Protection Agency, The Estimated Recovery Potential of Conventional Source Domestic Crude Oil, May 1975.

In the large project, a factor of 70 percent was assigned to the field to account for conditions which could tend to limit operation in parts of the field such as shaled-out reservoir or variations in sweep efficiency. Over the life of a field, oil production will tend to decline and the ratio of steam to oil produced will increase so that steam generating capacity and output is assumed to remain constant throughout the project.

6.2.1.2 "Small" Project Case

The second case represents smaller isolated oil fields such as the domed or anticline structures amenable to thermal oil recovery which are located throughout the Rockies. Similar dispersed small-scale projects are also likely to exist in oil fields elsewhere in the country. The density of such projects would vary greatly by region.

The data shown on Table 6-1 are characteristic of ongoing small projects. For example, Amoco operates a project at Winkleman Dome in Fremont County, Wyoming which has boiler capacity to process 4,180 barrels of water to approximately 111,000 barrels of steam per day.[1] Assuming 1,000 psia and 80 percent quality steam is generated, 1,734 million Btu's per day (289 barrels of oil at 6 million Btu's per barrel) is required or 90 million Btu's per hour at 80 percent efficiency. It is reasonable to assume that a stream factor of 90 percent may be applied to the boilers so that 100 million Btu's per hour of installed capacity would be required. This project produces about 850 barrels of oil per day for each 289 barrels of fuel burned for an oil production to fuel ratio of 2.95:1.

6.2.1.3 Development Patterns

In the large project case, it is assumed that the density of boilers simultaneously in operation resulted from a number of operators in the oil field independently arriving at similar development decisions. It is recognized that the early phases of a steam displacement project involve empirical application of the technology. Following pilot studies, a few boilers are operated in project patterns and reservoir response is determined. The data are evaluated and additional steam generating capacity is added to the project patterns if the economics of the expansion appear to be favorable.

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[1] "Winkleman Dome Steam-Drive Project Expands," Oil and Gas Journal, (October 21, 1974): 116.

The locations of steam generating units were as follows in the modeled projects. For the small project two 50 million Btu per hour boilers were located at the middle of the field adjacent to each other. In the large project, two 50 million Btu per hour generators and a 20 million Btu per hour generator were assumed to be located at the center of each quarter section.

Actual development patterns of steam generators in a particular field will depend upon the following: historical precedent; terrain; location of existing roads, pipelines and other facilities; shape of operator's lease or unitized area; and the results of pilot scale development projects. In addition, the location of steam generators in large-scale planned developments may be selected on the basis of a trade-off analysis of heat losses, boiler costs, location of water sources and other factors. Boiler sizes selected are typical of those used in large-scale developments now underway at Kern River, South Belridge, Mt. Poso and elsewhere. In these projects, 50 million Btu/hr units are the standard unit of steam generating capacity. This size unit appears to have become standard because of its high efficiency, operating flexibility, and other factors. The presence of 20's in the large project case represents pilot scale capacity which preceded full-scale development.

6.2.1.4 Geographic Locations

Meteorological conditions were selected to represent the three regions of the country where most of the thermal oil recovery will take place. The Central Valley of California was characterized by weather data from Bakersfield, California, supplemented with data from Los Vegas, Nevada. The Northern Rockies were represented by meteorological data from Lander, Wyoming. Meteorological data from Shreveport, Louisiana was used to characterize the inland Gulf Coast region.

6.2.2 Pollutant Emission Rates

The following discussion presents the pollutant emission rates from steam generating units used in this assessment of the air quality impacts and the boiler operating characteristics upon which these rates are based.

Data on the operating characteristics of the steam generators for thermal displacement were obtained from discussions with staff engineers at the original equipment manufacturers and at the oil companies currently operating the units. The pollutant emission rates from the steam generators were calculated from data from source sampling reports submitted by several oil companies to state air pollution control agencies and from design specifications of the generators. The operating characteristics used for this analysis are summarized in Table 6-3.

The operating characteristics used in the analysis are representative of generators currently operating in rural area oil fields. Almost all of the generating units burn crude oil with a large amount of excess air. Residual fuel oil is burned in other generators with the same operating conditions. The units which are designed to operate from 10 to 30 percent excess air generally operate in the field at nearly 30 percent excess air.

The generators generally have a design efficiency of 88 percent and have both radiative and convective boiler tube sections. The design steam output is 80 percent quality (80 percent vapor) steam at 2,000 psig and 1,045 Btu per pound. The design flue gas temperature ranges from 350° to 400° F. However, because particulates collect on boiler tubes, the units operate in the field with flue gas temperatures between 400° to 600° F. The flue gas is generally released from a "stub" directly above the convection section of the boiler. Because of the large cross-sectional area of the stub, the flue gas has a low exit velocity. The height of release of the flue gas is only a few meters above the ground. Stacks can be added to the sub of the generating units.

The major pollutant emissions from the oilfield steam generators are sulfur dioxide, nitrogen oxide, and particulates. Hydrocarbons and carbon monoxide are emitted in minor quantities. The pollutant emission rates assumed for the study are summarized in Table 6-4.

6.2.2.1 Sulfur Dioxide

The sulfur dioxide emissions rate from the generators is dependent on the sulfur content of the fuel. Crude oil is used as fuel in most steam generators because little if any natural gas is produced or available for enhanced recovery

TABLE 6-3

SUMMARY OF OILFIELD STEAM GENERATORS OPERATING CHARACTERISTICS

HEAT OUTPUT (MM Btu/hr)	HEAT INPUT (MM Btu/hr)	VENT HEIGHT (M)	EQUIVALENT STACK DIAMETER (M)	FLUE GAS EXIT[a] (M/Sec)	STACK TEMPERATURE (C)
20	22.6	3.96	1.04	2.67	260
50	56.2	6.0	1.54	5.87	260

[a] Gas Exit velocity based on firing with 30 percent excess air and fuel with a heating value of 153,500 Btu per gallon.

TABLE 6-4

SUMMARY OF EMISSION RATES FOR STEAM GENERATORS

STEAM GENERATOR SIZE	HEAT INPUT (barrels of oil per day)	SO_2 (gm/sec)	NC_X (gm/sec)	PARTICULATES (gm/sec)	HYDROCARBONS (gm/sec)	CO (gm/sec)
20 MM Btu/hr	22.6	2.98	1.33	0.22	.04	0.01
50 MM Btu/hr	56.2	7.37	3.29	1.10	.11	0.02

[a] The emission rates calculated based on units combusting oil having one percent sulfur and 153,500 Btu per gallon with 30 percent excess air.

operations. Furthermore, the logistics of distributing fuel oils from the refinery back to the oil fields can be more complicated and costly than drawing off a part of the crude oil for use as fuel before selling the rest. In California, the shallow reservoirs which are amenable to steam displacement generally contain crude oil with a high sulfur content. The sulfur content of low gravity crudes ranges from 0.25 to 6 percent, with an average sulfur content for all fields in California of 2.1 percent. It is assumed that oil with a 1 percent sulfur content is characteristic of the fuel that will be used in the typical large project in the near future. The sulfur content of the oil from typical small projects was assumed to be 1.23 percent based upon the average sulfur content in oils from Wyoming fields that appear to be amenable to steam displacement.

6.2.2.2 Oxides of Nitrogen

The emission rate of nitrogen oxide is assumed as 3.0 pounds per barrel of oil burned. The data obtained from one oil company gave an emission rate of 1.8 pounds of NO_2 per barrel of fuel burned. From data on horizontally-fired steam generators, an emission rate of 3.0 pounds per barrel appears to be more realistic.[1,2]

6.2.2.3 Particulates

The particulate emission rate which was observed by two oil companies was 0.5 pounds per barrel of fuel.[3] This value is used as the particulate emission rate for the study. Several factors may affect particulate emissions including trace metal content of the crude oil. Characterization of these emissions is beyond the scope of this work.

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[1] Process Research, Inc., Air Pollution from Fuel Combustion in Stationary Sources, for the U.S. Environmental tection Agency, Report No. EPA-R2-73-241, October 1972.

[2] U.S. Environmental Protection Agency, Compilation of Air Pollutant Emission Factors, AP-42, April 1973.

[3] Personal communication with Kern County Air Pollution Control District, Bakersfield, California.

6.2.2.4 Hydrocarbons

The emission rate of hydrocarbons from the oil-fired steam generators is reported as 0.1 lbs/barrel of fuel in source tests from one oil company.[1] Fugitive emissions of hydrocarbons from other point and area sources in oil fields have not been characterized and are not included in the analysis.

6.2.2.5 Carbon Monoxide

The carbon monoxide emission rate from steam generators is approximately 0.02 lb/barrel.[2] Even though the emission rate is much lower than other similar types of oil-fired generators, the estimate appears realistic because the oil-field units use a large amount of excess air for combustion.

6.2.3 Modeling Procedure

The air quality impact of development of the "typical" steam displacement projects is predicted using two EPA air quality models: the Climatological Disperson Model (CDM) and CRSTER. The CDM calculates the mean annual concentration from many point and/or area sources, while the CRSTER models the 1-hour, 24-hour, and annual concentration from a single source. Both models use Briggs' formulae to calculate plume rise. The analysis assumes that the oil field and surrounding territory is on flat terrain.

The maximum 3-hour concentration was calculated by assuming the maximum one hour concentration persisted for three hours. The maximum 24-hour concentration and the mean annual concentration are calculated by the model. The annual transport concentration of SO_2 is calculated by using the CDM.

The increase in ambient air concentrations from the "typical" small project was predicted by CRSTER using 1964 hour-by-hour surface observation data and measured height data for Lander, Wyoming.

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[1] Chemecology Corporation, Steam Generator Testing: Kern River, Bakersfield, Report No. 230, December 1974.

[2] Chemecology Corporation, Steam Generator Testing, December 1974.

The assessment of the air quality impact of the "typical" large project required two modeling approaches. A modular approach is used to predict the maximum 3-hour and 24-hour ambient air concentrations. The CRSTER calculated the SO_2 and particulate ground level concentration from 0.3 to 4.3 km away from one group of generators. The day, direction and location of the maximum 24-hour SO_2 concentration outside the field was determined for a group of generators nearest to the oilfield boundary. The rows of the groups of the generators were aligned in the direction of the maximum 24-hour concentration. Total maximum 24-hour SO_2 concentration from operation of all the generators in the field was calculated by summing contribution of all the groups of the generators to the predicted site of maximum concentration for the 24 hours.

The maximum 3-hour SO_2 concentration from steam generators was calculated by assuming that the conditions that caused the highest 1-hour concentration outside the field persisted for three hours. The maximum 1-hour concentration was determined using the procedure described for calculating the maximum 24-hour concentration. The annual average concentration and the concentration at large distances from the source were determined using a direct modeling approach. The CDM predicted the mean annual SO_2 and particulate concentrations for receptors located in telescoping grids.

6.3 Discussion of Results

6.3.1 Dispersion of Pollutants (Uncontrolled Case)

The results of the dispersion modeling are plotted on maps to show the concentration isopleths of sulfur dioxide at ground level in ambient air outside the oil field. Figures 6-1 to 6-3 illustrate the isopleths from the large project case burning 1 percent sulfur fuel under meteorological conditions for three regions. Figures 6-4 to 6-7 show the sulfur dioxide isopleths from CDM modeling of the small project case. Figure 6-8 shows the results for CRSTER modeling. Figures 6-9 and 6-10 illustrate the NO_x isopleths of the small project case.

Standard steam generating units have a low height of emission release and low flue gas exit velocity. Because of

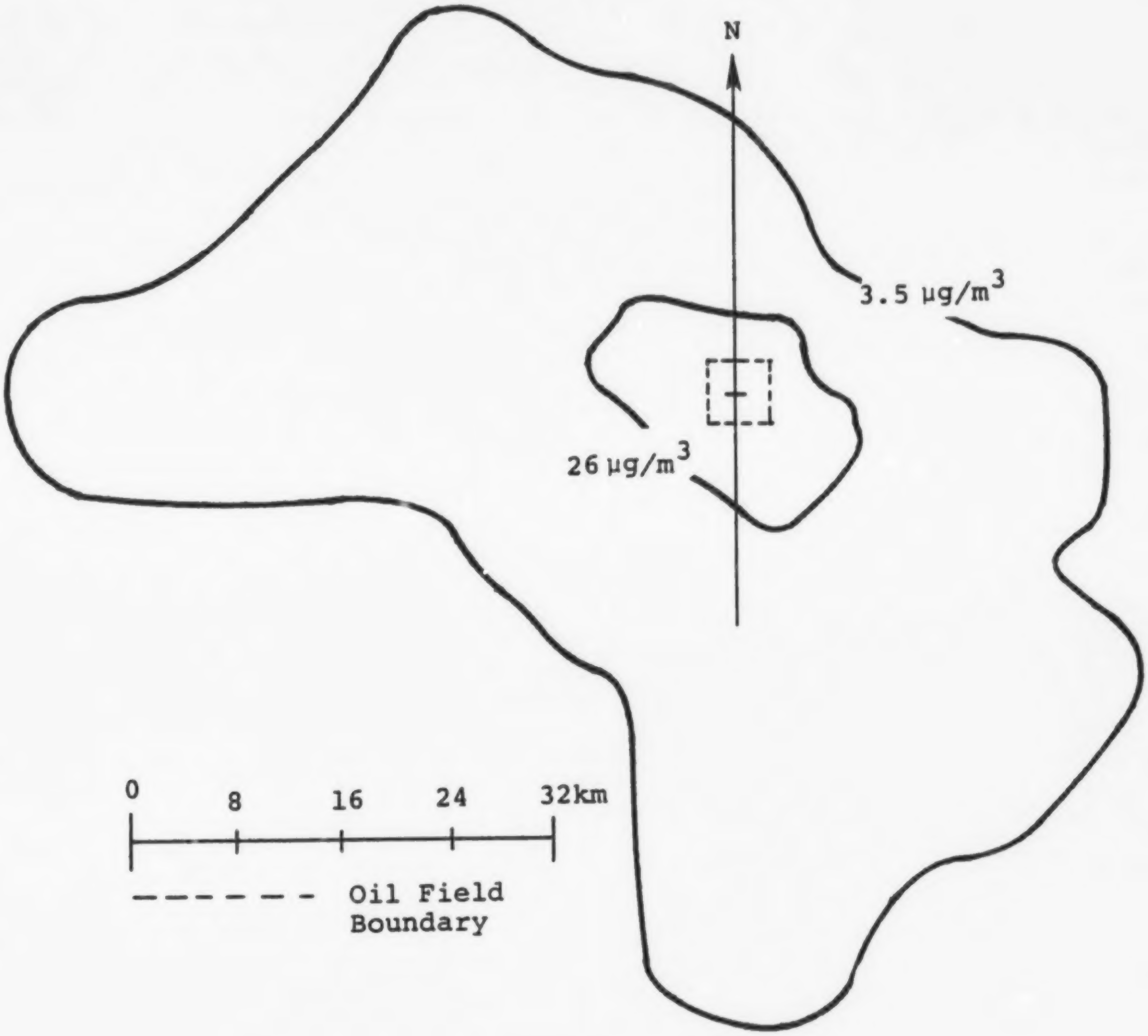
N
3.5 μg/m³
26 μg/m³
0
8
16
24
32km
Oil Field Boundary

Figure 6-1. This figure displays the Annual SO_2 Isopleths for Full Scale Development of a "Typical" Large Project for Thermal Oil Recovery in Inland California. (Sulfur content in fuel = 1.0 percent; Meteorological Data: Bakersfield, CA; Dispersion Model: CDM)

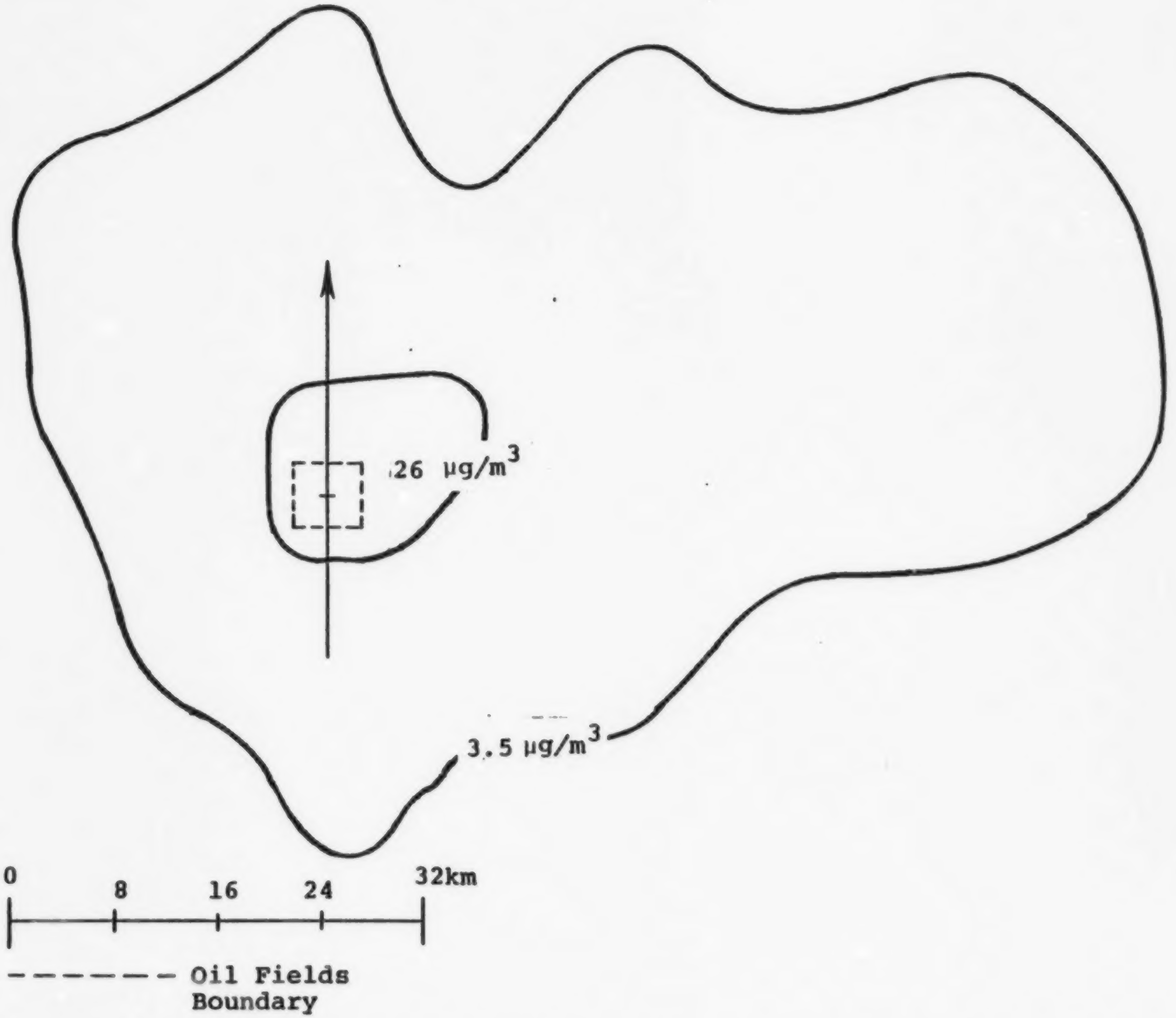
26 μg/m3
3.5 μg/m3
0
8
16
24
32km
Oil Fields Boundary

Figure 6-2. This figure displays the Annual SO_2 Isopleths for Full Scale Development of a "Typical" Large Project for Thermal Oil Recovery located in the Northern Rockies. (Sulfur content in fuel = 1.0 percent; Meteorological Conditions: Lander, WY; Dispersion Model: CDM)

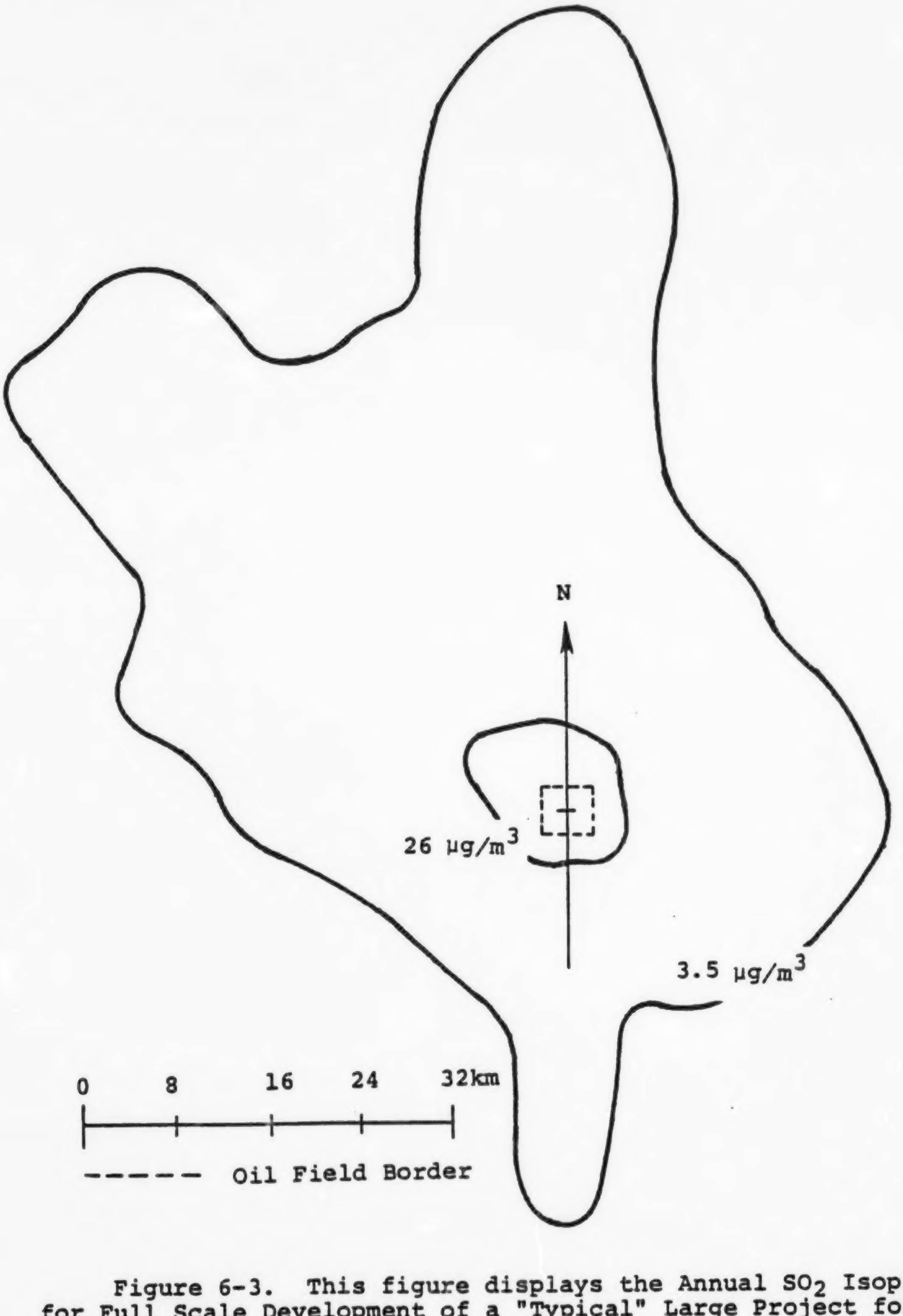
N
26 μg/m3
3.5 μg/m3
0
8
16
24
32km
----- Oil Field Border

Figure 6-3. This figure displays the Annual SO_2 Isopleths for Full Scale Development of a "Typical" Large Project for Thermal Oil Recovery in the Inland Gulf Coast. (Sulfur content in fuel = 1.0 percent; Meteorological Data: Shreveport, LA; Disperson Model: CDM)

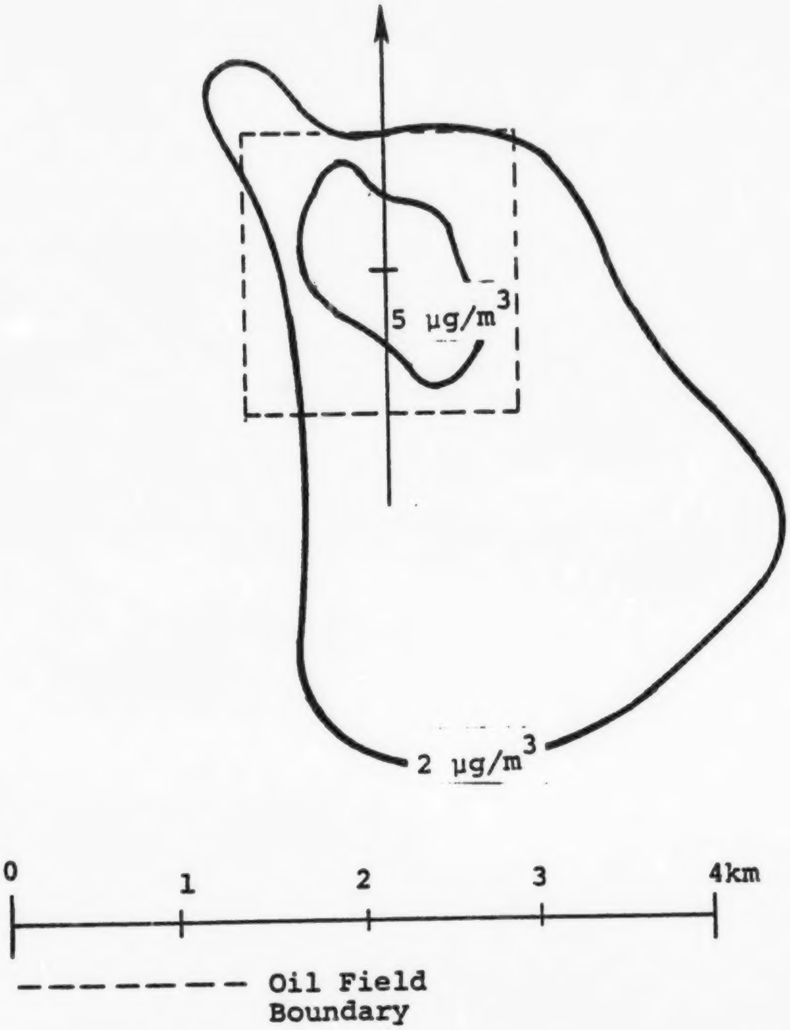
5 µg/m3
2 µg/m3
0
1
2
3
4km
Oil Field Boundary

Figure 6-4. This figure displays the Annual SO$_2$ Isopleths for Thermal Oil Recovery for "Typical" Small Project Field in Inland Calfornia. (Fuel Sulfur Content: 1.23 percent; Meteorological Data: Bakersfield, CA; Dispersion Model: CDM)

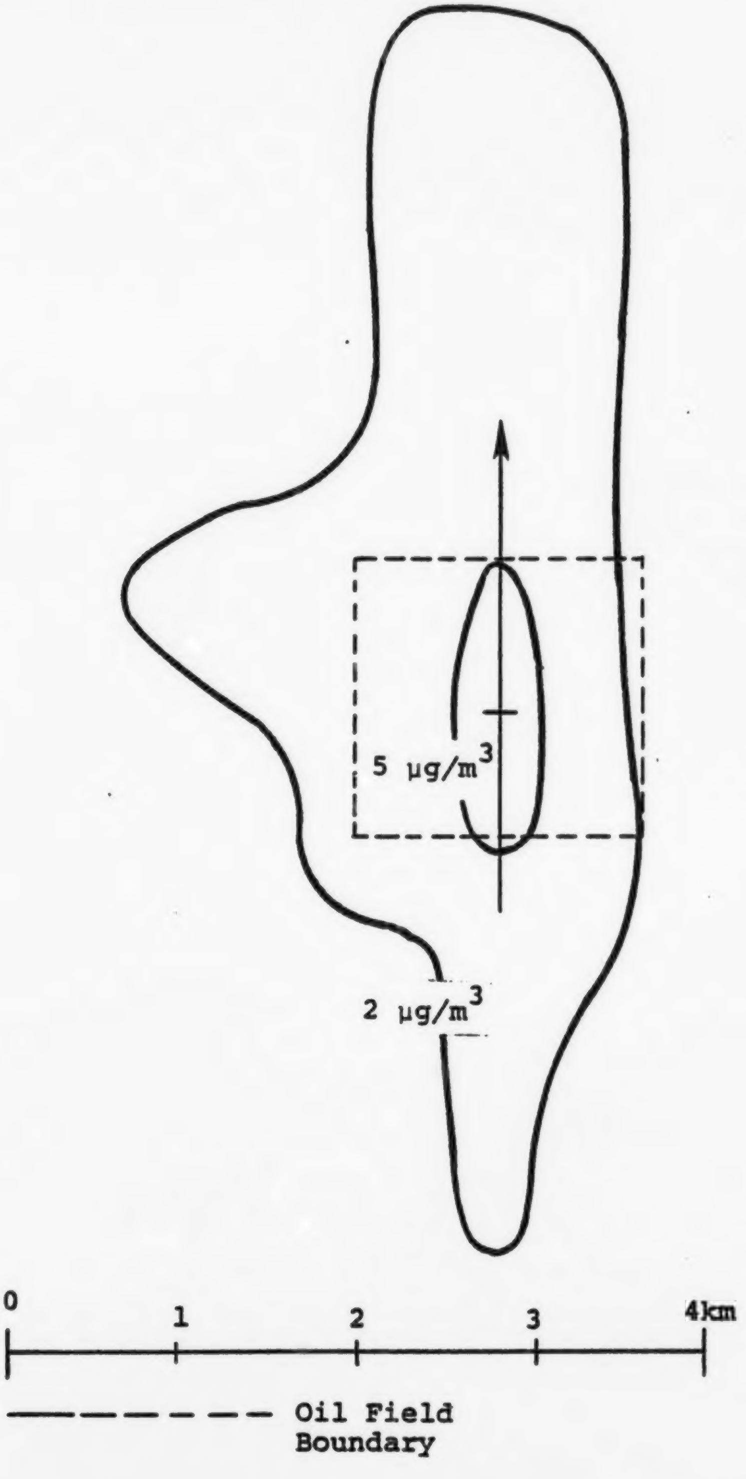
5 μg/m³
2 μg/m³
0
1
2
3
4km
Oil Field Boundary

Figure 6-5. This figure displays the Annual SO_2 Isopleths for Thermal Oil Recovery for "Typical" Small Project Field in the Inland Gulf Coast. (Fuel Sulfur Content: 1.23 percent; Meteorological Data: Shreveport, LA; Dispersion Model: CDM)

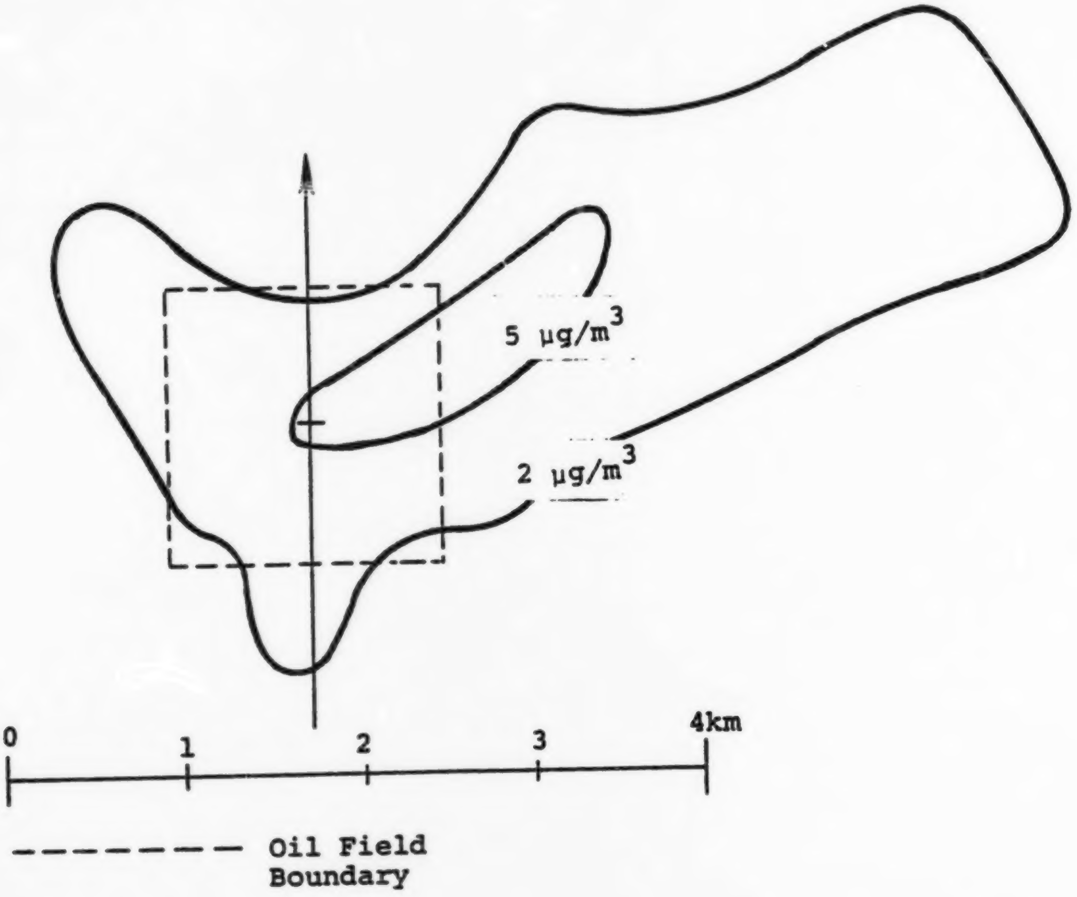
5 μg/m³
2 μg/m³
0
1
2
3
4km
Oil Field Boundary

Figure 6-6. This figure displays the Annual SO_2 Isopleths for Thermal Oil Recovery for "Typical" Small Project Field in Northern Rockies. (Fuel Sulfur Content: 1.23 percent; Meteorological Data: Lander, WY; Dispersion Model: CDM)

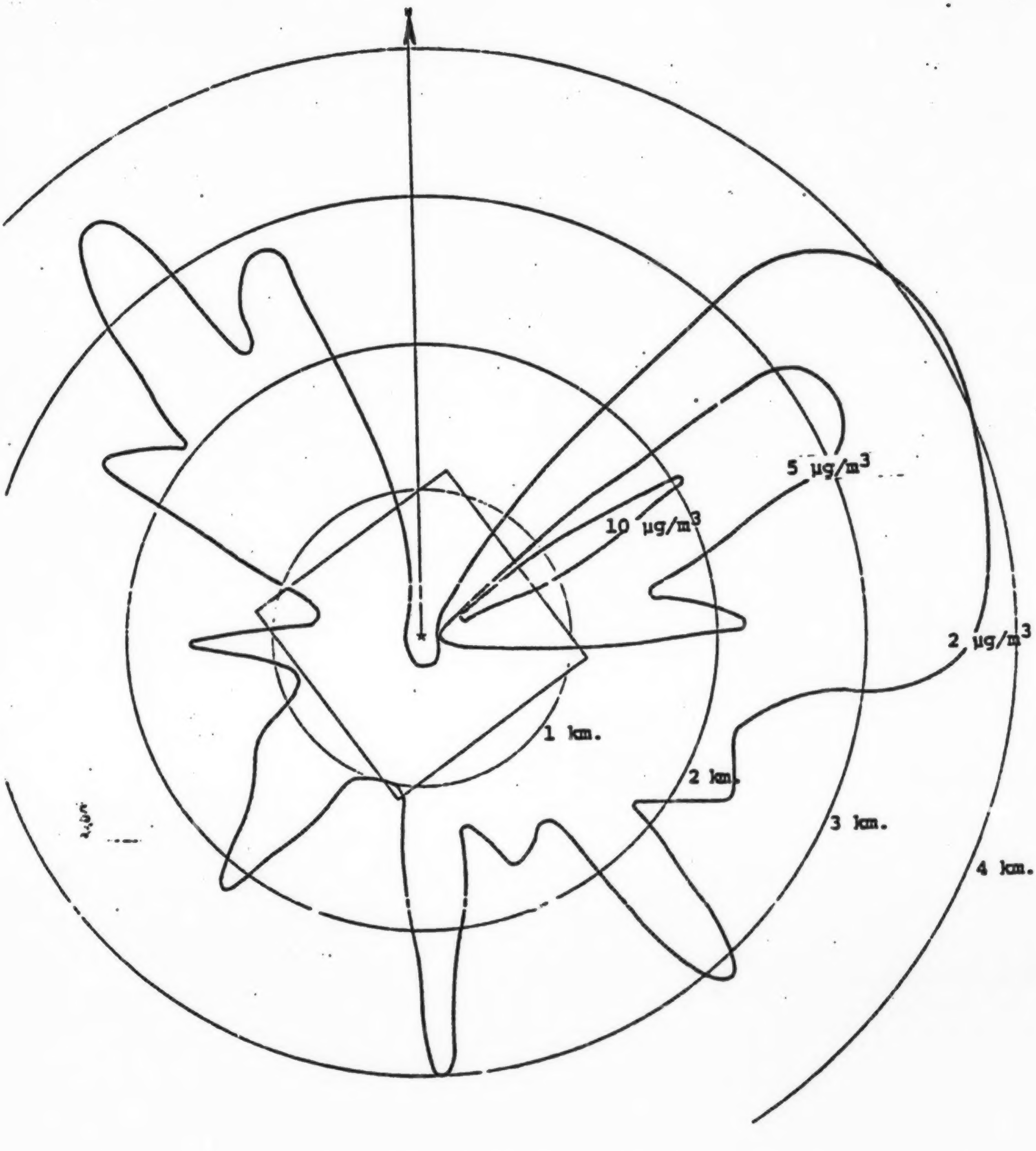

Figure 6-7. This figure displays the Annual SO_2 Isopleths for Full Scale Development of a "Typical" Small Project for Thermal Oil Recovery in the Northern Rockies. (Fuel Sulfur Content: 1.23 percent; Meteorological Data: Lander, WY: Dispersion Model: CRSTER)

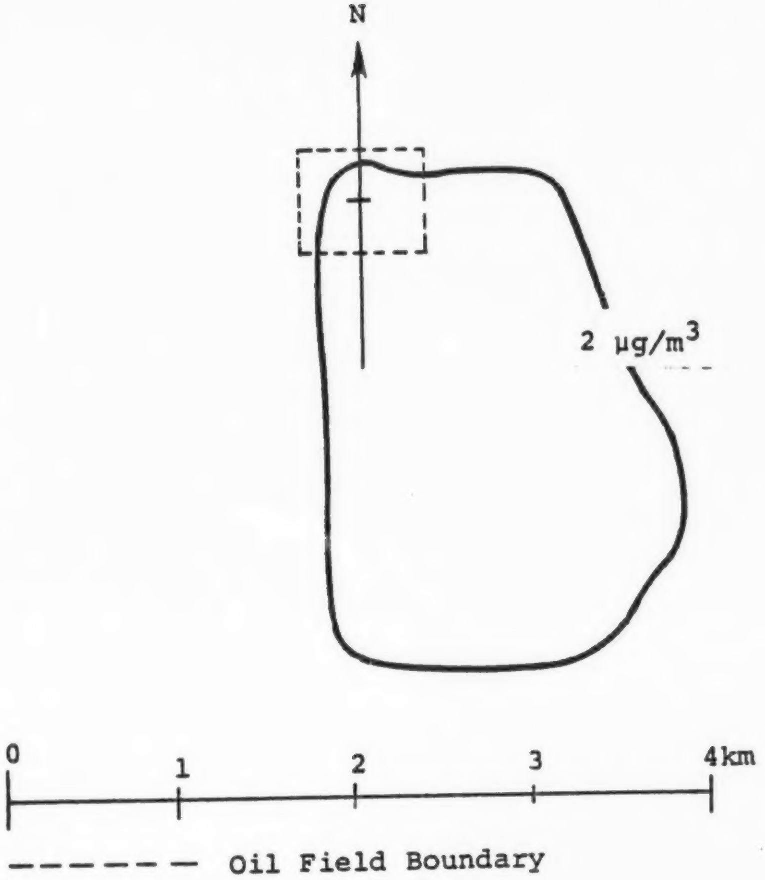
N
2 µg/m3
0
1
2
3
4km
------ Oil Field Boundary

Figure 6-8. This figure displays the Annual NO_x Isopleths for Thermal Oil Recovery in a "Typical" Small Project Field in Inland California. (Fuel Sulfur Content: 1.23 percent; Meteorological Data: Bakersfield, CA; Dispersion Model: CDM)

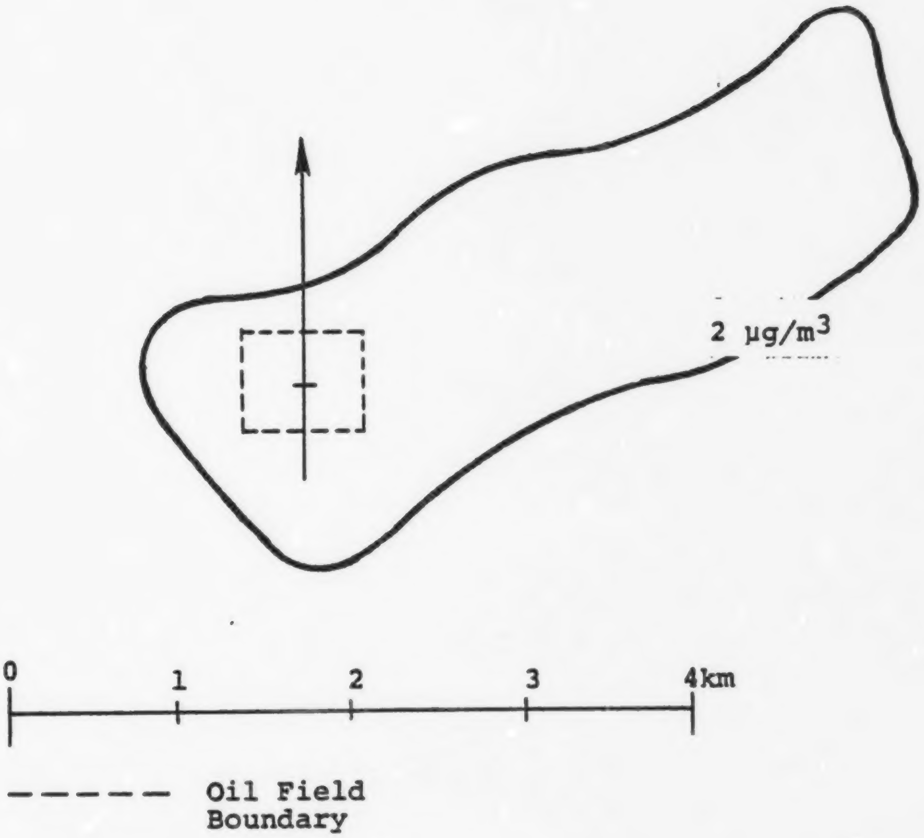
2 µg/m³
0
1
2
3
4km
Oil Field Boundary

Figure 6-9. This figure displays the Annual NO_x Isopleths for Thermal Oil Recovery in a "Typical" Small Project Field in the Northern Rockies. (Fuel Sulfur Content: 1.23 percent; Meteorological Data: Lander, WY; Dispersion Model: CDM)

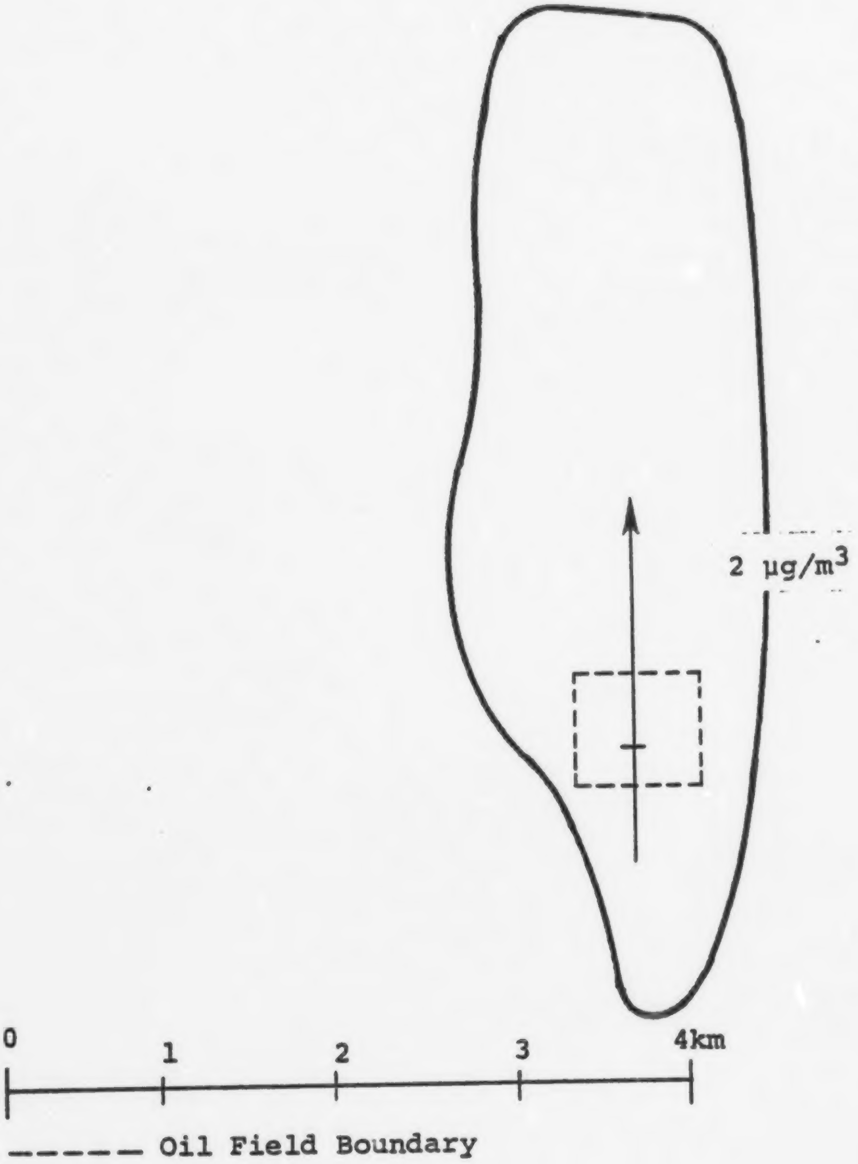
2 µg/m³
0
1
2
3
4km
----- Oil Field Boundary

Figure 6-10. This figure displays Annual NO_x Isopleths for Thermal Oil Recovery in a "Typical" Small Project Field in the Inland Gulf Coast. (Fuel in Sulfur Content: 1.23 percent; Meteorological Data: Shrevesport, LA; Dispersion Model: CEM)

these characteristics, the maximum short-term ground concentration occurs during neutral atmospheric stability and high wind speed conditions at the boundary of the oil field and during fumigation conditions caused by breaking up of ground based inversions. The concentration rapidly decreases further from the oil field but can be above 26.5 micrograms per cubic meter as far as 11 kilometers from the oil field and 3.5 micrograms per cubic meter 68 kilometers from the project depending on local meteorological conditions.

The small thermal oil recovery project was able to meet air quality standards outside the oilfield boundary. However, large projects exceeded the annual and 24-hour standards for sulfur dioxide.

6.3.2 Emission Control to Meet National Ambient Air Quality Standards

The analysis presents the level of emission control required for two typical cases to meet the NAAQS. It should be noted that the operation of thermal oil recovery in an area may preclude the development of other energy producing facilities.

The numerical limits for the National Ambient Air Quality Standards are shown in Table 6-5. The predicted increases in ambient air concentration of SO_2 and particulates from the development of the two typical projects with steam generators burning the 1 percent sulfur content crude oil are compared to the standards. The amount of emission reduction required is calculated as follows:

$$\% \text{ Reduction} = \frac{X_p - X_s}{X_p} \times 100 \qquad (6\text{-}1)$$

where X_p equals the predicted increase in ambient air concentration of the pollutant and X_s equals the standard for the pollutant. The sulfur content of the steam generators fuel that will enable the case to meet the ambient air quality standards is calculated as follows:

$$S_s = \frac{X_s}{X_p} \times S_p \qquad (6\text{-}2)$$

TABLE 6-5

EMISSION REDUCTION REQUIRED TO MEET NATIONAL AMBIENT AIR QUALITY STANDARDS FOR FULL-SCALE DEVELOPMENT OF THERMAL RECOVERY FOR A "TYPICAL" LARGE FIELD IN INLAND CALIFORNIA

(Base Case is for % sulfur fuel, numbers in parenthesis assume steam generators must meet a NSPS of 0.8 pounds of sulfur dioxide per MM Btu.)

POLLUTANT STANDARD	MAXIMUM PREDICTED CONCENTRATION FROM THE FIELD ($\mu g/m^3$)		EPA AMBIENT AIR QUALITY STANDARDS ($\mu g/m^3$)	POLLUTANT EMISSION REDUCTION TO MEET REGULATION (Percent)		MAXIMUM SULFUR CONTENT IN FUEL TO MEET STANDARD (Percent Weight)	
	Base Case	NSPS		Base Case	NSPS	Base Case	NSPS
Sulfur Dioxide							
Annual	140	(96)	80	43	(17)	0.57	(0.57)
24-Hour[a]	460	(315)	365	21	(--)	0.79	(--)
3-Hour[a]	662	(452)	1,300	--	(--)	--	(--)

[a] The 24-hour and 3-hour standards are not to be exceeded more than once a year.

where S_a equals the sulfur content of the fuel required to meet the applicable air quality standard for the class and S_p equals the assumed sulfur content of the oil burned in the generator without air pollution controls.

6.4 Regulations and Emission Controls Strategies

6.4.1 Present Source Regulation

The steam generators used in thermal oil recovery are not required to meet New Source Performance Standards (NSPS). The largest oil field steam generator is 240 MM Btu/hr, which is slightly less than the minimum size (250 MM Btu/hr) regulated by the NSPS.[1] Furthermore, State Implementation Plans generally permit the use of high sulfur fuel (2.0 percent or greater) in the fuel limitations for rural areas in which most oil fields amenable to thermal recovery are located. In urban areas, stricter fuel limitations are imposed on the operators.

The NSPS for boilers in utility service is 0.80 pounds of sulfur dioxide per million Btu's.[2] As shown in Table 6-4, the emission rates for 20 MM Btu and 50 MM Btu steam generators burning 1 percent sulfur fuel are approximately 1.17 pounds per million Btus. Therefore, if this NSPS were also applied to oilfield steam generators, emissions would be limited to the equivalent of about 0.68 percent sulfur fuel. As shown on Table 6-5, such a performance standard would still cause the annual NAAQS to be violated.

6.4.2 Emission Control Strategies

A number of control alternatives are available to the operator of thermal oil recovery to meet National Ambient Air Quality Standards in large oil fields where concentrated development similar to the large project case modeled here could occur. These strategies include: (1) installation of taller stacks on each of the boilers to increase flue gas exit velocity and height of emission release, (2) combining emissions from several boilers into a single stack to increase momentum flux of the plume and height of emission release, (3) combustion of lower sulfur fuel to reduce total SO_2 emissions, and (4) flue gas desulfurization to reduce total SO_2 emissions with the possibility of also reheating the exhaust gas to augment plume rise. These control strategies may be employed individually or in combination to enable the project to meet air quality standards. Each of these control alternatives presents advantages and disadvantages in terms of economic, energy and environmental impacts. The assessment of the impacts of these control alternatives requires site-specific analysis of the costs and efficiency of extraction and the control systems which is beyond the scope of this study.

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[1] 40 CFR 60, Subpart D, §60.40.

[2] 40 CFR 60, Subpart D, §60.43(a)(1).

6.5 Limits of Analysis

Assessment of the impact of individual projects for thermal oil recovery on ambient air quality requires site-specific analysis. The increase in ambient air concentration of pollutants in the vicinity of the field and the dispersion of the emissions from a field into adjacent areas will depend on terrain, local meteorology, and the operations, the emission characteristics, and the distribution of the steam generators in the field.

The assumptions and dispersion models were selected for the analysis so that impact of thermal displacement oil recovery on ambient air quality was not overstated. The following factors were not included in this preliminary assessment and could affect the air quality impacts of thermal recovery.

6.5.1 Terrain

The "typical" projects are assumed to be on flat terrain. A small increase in ground elevation in the vicinity of the field can drastically increase the impact of the field on local ambient air quality because the oilfield steam generators currently operated generally have low heights of emission release (10.6 m or less) and low flue gas exit velocities.

6.5.2 Sulfur Content in Fuel

The impact of the SO_2 emissions on ambient air quality can be expected to be higher than predicted in the analysis if the steam generators of present design continue to be installed and operated. For example, the assumed SO_2 emission rate for the "typical" large project is based on fuel sulfur content of 1 percent, which is representative of reservoirs currently being developed, whereas the average sulfur content of crudes in all fields amenable to thermal oil recovery in California is approximately 2 percent with a maximum in excess of 6 percent. Present emission limitations for rural areas in California would permit combustion of up to 2 percent sulfur crude oil.

6.5.3 Development Pattern

The assumed uniform density and spacing of the generators in a large project probably understates the impact of the field on ambient air quality. Since the reservoir characteristics are not uniform throughout a field, it may be more realistic to assume that a number of generators may be grouped in one location and/or may be placed near the perimeter of a field. Such development patterns would result in higher ambient air concentrations than predicted in the analysis. Currently, several projects in California have five to ten 50 MM Btu/hr units grouped for operation and some are close to the boundary of the field.

6.5.4 Modeling

The EPA-developed gaussian models tend to overestimate the plume rise under high wind speed conditions. The emissions from steam generators have maximum impact on ambient air quality when neutral atmospheric stability and high wind speeds cause a small rise in the plume. Because the plume is released close to the generator, during high wind speeds an aerodynamic wake is formed around the generator. The wake forces the plume toward the ground, causing much higher ground concentrations than predicted by the gaussian dispersion models.

6.5.5 Site Classification

Another issue in the assessment of the impact of thermal displacement oil recovery on ambient air quality is whether or not an oil field is considered an industrial site. Two policies have been used by EPA to define the maximum ground concentration from industrial sources. The first criterion for calculating the maximum ambient air concentration from a source is to determine the highest concentration measured at the boundary of the industrial property. The other criterion for determining the maximum ambient air concentration from a source is to measure or predict the maximum concentration for any site which the population has reasonable access, such as the road through private land.

The first criterion is difficult to apply to oil fields because the site controlled by an oil company may not be easily defined since surface rights and mineral rights may belong to different owners. In the large field in which several oil companies operate the thermal displacement projects, it is not clear if the first criterion is applied at the boundary of the area owned by a specific oil company or the boundary of all land owned or controlled by the oil companies operating in a given oil field.

The second criterion will depend upon the specific site. Although it is reasonable to assume that people may have a free access to the large oil fields, it is unlikely that people will use the fields for recreational purposes for example. However, in some instances, houses and public highways may be located within or traverse oil fields amenable to thermal oil recovery such as oil fields located in the Los Angeles Basin.

CHAPTER SEVEN

POLICY RECOMMENDATIONS

7.1 Summary of Problem Areas

The focus of the study is upon those potential environmental problems which are unique to tertiary oil recovery as opposed to the environmental problems which have the same types and incidence as in conventional petroleum extraction operations. A comparative analysis of the industry's past performance in environmental protection was not within the scope of the effort. The potential impacts of tertiary oil recovery are upon water quality, water supplies and air quality as discussed below.

7.1.1 Water Supplies and Quality

Two potential causes of water quality deterioration during tertiary oil recovery are most significant. These causes are: (1) spills of chemicals as a result of transportation and handling, and (2) improper disposal of chemically-loaded produced brine to surface waters. Both of these factors are difficult to mitigate by further regulation.

Operational tertiary recovery projects are likely to pose few hazards to underground water supplies because numerous physical and chemical processes such as adsorption, partitioning, precipitation, dilution, entrapment, and bacterial or chemical degradation tend to reduce greatly the concentration of chemicals from a leak or spill. At present, among commonly-used materials, petroleum sulfonate surfactants could have the most adverse impact on water supply quality. However, these materials are susceptible to adsorption and precipitation as much or more than any other chemical used. New chemicals for use in tertiary oil recovery may have fewer adsorption tendencies and such developments should be closely monitored by EPA.

Despite the fact that additional mechanisms associated with well age tend to increase the chances of leaks, the possibility of future impacts upon water supplies from completed projects should be of the same small magnitude as the risks from ongoing recovery projects. The mitigating processes act upon contaminants in an aquifer.

7.1.2 Air Quality

Widespread development of steam displacement projects to recover low gravity crude oils in shallow reservoirs could have a significant impact on air quality. The limits on sulfur content in fuels set forth in many state implementation plans are not adequate to prevent ambient air quality standards for sulfur dioxide from being exceeded. A variety of control strategies are available which may make it possible to keep air quality within the standards despite high-density development of this thermal oil recovery technique. However, the control strategy which is selected or required may limit the development of this petroleum resource and curtail the quantity of oil economically recoverable from the oil field.

Air quality problems may also arise as a result of on-site manufacture of petroleum sulfonates and due to fugitive emissions of vaporous hydrocarbons at thermal oil recovery projects and of hydrogen sulfide at miscible gas displacement projects.

Emissions from many sources in tertiary oil recovery projects have not been adequately characterized. It is important to consider reservoir characteristics and recovery process variables in the development of emission factors and the drafting of environmental policies to control undesirable discharges.

7.2 Current Environmental Regulatory Framework

7.2.1 Water Pollution

EPA's present authority over tertiary oil recovery operations is limited because of two provisions of the Safe Drinking Water Act. First, the states have until December 1977 to submit programs for underground injection. Secondly, Section 1421(b)(2) provides that regulations under this act cannot interfere with or impede wells for oil and gas production "unless such requirements are essential to assure that underground socurces of drinking water will not be endangered." However, there are still several areas in which EPA can exercise some authority or oversight. Section 1424 provides for interim regulation of underground injections if an area within a state is designated by the Administrator as one in which no new underground injection well may be operated until the applicable underground injection control program takes effect. A permit for the operation of such wells may be issued by the Administrator. The criterion for designating such an area is that only one aquifer is the sole or principle drinking water source for the area and which, if contaminated, would create a significant hazard to public health. For example, the Edwards aquifer may qualify parts of South Texas under this section.

The Administrator also has the authority to issue permits in designated areas for new injection wells. The permit may require the use of such control measures as necessary to assure that the operation of the well will not contaminate the aquifer of the designated area in which the well is located. This may not sound like a particularly relevant provision because tertiary recovery is not often carried out in "new wells," but a "new underground injection well" is defined by the Act as one whose operation was not approved by appropriate state and Federal agencies before the date of the enactment of this title. Therefore, some of the very old wells may not have state or Federal permits, and would qualify as "new wells."

Under Section 1424(e) operators might apply for Federal finance assistance for projects in designated areas to assure that the aquifer is not contaminated.

Complaints of well water contamination are filed with various state regulatory commissions. For example, seven complaints of groundwater pollution were filed with the Texas Railroad Commission. If appropriate state action is not forthcoming to deal with endangerment of health and a contaminant is believed to be present, the Administrator may take such actions under the Act as he may deem necessary to protect health. In particular, the Administrator may apply for a restraining order or temporary injunction against the operator causing the contamination. Via Section 1431, therefore, EPA can deal with any acute pollution situation that may arise from tertiary recovery.

Though this provision is useful in dealing with contaminant sources such as improper surface disposal of produced brine and chemical spills, it is ineffective in mitigating the impact of a polluted aquifer. As discussed in Chapter Five, there can be a time lag between the polluting event and appearance of the contaminant at a drinking water source. An effective environmental policy must, therefore, anticipate contaminant sources before the pollution of an aquifer occurs. For example, operators of tertiary oil recovery projects could be required to investigate for old abandoned, poorly plugged wells within the area of their project before recovery operations can begin. Old wells which are found to penetrate possible drinking water sources could then be properly plugged before the project starts and the risks of pollution would be minimized.

Finally, under Section 1445, EPA has the opportunity to promulgate a wide variety of regulations for anyone who may be subject to an applicable underground injection control program or who may be subject to the permit requirement to Section 1424. According to this section, EPA can require such persons to maintain records, make reports, monitor and provide information as the Administrator may reasonably require by regulation to assist him in establishing regulations. These requirements could be invoked in the event that a voluntary program of information exchange to monitor the types of materials under consideration for use in tertiary oil recovery does not succeed.

This Section also has provisions for the confidentiality of information collected if it would in any way divulge trade secrets or secret processes making the legislation particularly helpful if it is to be applied to petroleum companies that may utilize proprietary tertiary recovery processes or materials.

7.2.2 Air Pollution

It is unclear whether some enhanced recovery emissions sources represent existing sources or a new source which would be subject to New Source Performance Standards (NSPS). It can be argued that some tertiary recovery sources represent a modification to an existing source which is defined as a new source in terms of New Source Performance Standards. Sulfonation units present an ambiguous problem. Some sulfonation units are constructed as part of refineries and are probably, therefore, covered by performance standards for refineries. A sulfonation unit that is constructed as part of a field operation, on the other hand, is probably not covered by refinery performance standards. Similarly, existing production wells which are subsequently utilized in steam displacement or *in-situ* combustion projects lack clear definition as type sources.

The steam generators used in steam displacement are not required to meet New Source Performance Standards. The largest oilfield steam generator is 240 million Btu/hr, which is slightly less than the minimum size (250 million Btu/hr) source regulated by the NSPS. The oil fields amenable to thermal displacement in rural areas are generally permitted to use of high sulfur content fuel (2.0 percent or greater) according to the fuel limitations established by State Implementation Plans.

Another issue in the assessment of the impact of thermal displacement oil recovery on ambient air quality is whether or not an oil field is considered an industrial site. Two policies have been used by EPA to define the maximum ground concentration from industrial sources. The first criterion for calculating the maximum ambient air concentration from a source is to determine the highest concentration measured at the boundary of the industrial property. The other criterion for determining the maximum ambient air concentration from a source is to measure or predict the maximum concentration for any site which the population has reasonable access to, such as the road through private land.

The first criterion is difficult to apply to oil fields because the site controlled by an oil company may not be easily defined since surface rights and mineral rights may belong to different owners. In the large field in which several oil companies operate the thermal displacement projects, it is not clear if the first criterion is applied at the boundary of the area owned by a specific oil company or the boundary of all land owned or controlled by the oil companies operating in a given oil field.

The second criterion will depend upon the specific site. Although it is reasonable to assume that people may have a free access to the large oil fields, it is unlikely that people will use the fields for recreational purposes for example. However, in some instances, houses and public highways may be located within or traverse oil fields amenable to thermal oil recovery.

Equitable development of steam displacement projects in oil fields within a region is another issue which is not addressed by present environmental policy and regulations. As discussed in the air quality impact analysis of a typical large project, NAAQS for annual average concentrations of sulfur dioxide are likely to be exceeded before an oil reservoir or a number of closely-spaced similar reservoirs can be fully developed. In the event that these resources are controlled by a number of operators, it is possible that the operator who first establishes steam displacement projects using steam generators without emission controls in a region can preempt development of projects by other oil producers. Similarly, the development of other types of energy facilities such as fossil fuel power plants will also be preempted.

7.2.3 State Oil Production Codes

The report identifies at least five areas in which state Codes impede tertiary recovery operations: (1) fluid injection, (2) well spacing, (3) allowables, (4) unitization, and (5) plugging. It would be useful to examine all the state Codes applicable to tertiary recovery. This legal survey would serve two useful purposes: (1) it would identify variations in state Codes which encourage or exclude tertiary recovery operations, and (2)it would point up inconsistencies in state laws that could be changed by individual states if they were aware of the loopholes or impediments presented to tertiary recovery.

It might be useful to hold a conference of state regulatory agencies concerned with oil and gas regulations. This conference would serve a wide variety of purposes. It would provide an opportunity for the states to learn of the projected future level of tertiary recovery operation to enable them to gauge how sizable future operations within their state may be. It will also provide a forum for EPA to explain to state officials the potential environmental risks that may be attributable to tertiary recovery operations. Finally, it would provide EPA a forum to explain to state officials steps that the states could take to ensure that they have sufficient authority in the area of tertiary recovery control.

7.3 Policy Recommendations

Additional research is required before specific regulatory measures, if any, can be identified. The involvement of and communication with state and regional oil and gas agencies such as discussed above would be an effective means of establishing regulations necessary to prevent possible environmental damage due to tertiary oil recovery. The forum described above will also be useful to identify areas where new Federal legislation may be needed.

The most significant issue which requires concise definition is a research program regarding environmental issues in tertiary oil recovery. Unanswered questions listed below under Research Needs regarding the possible environmental impacts of the processes should be addressed during the demonstration projects sponsored by the Energy Research and Development Administration. The EPA should obtain environmental data from such projects in sufficient detail so that variations in compositions of the discharges from tertiary oil recovery can be correlated with reservoir characteristics and process variables. Current policy should encourage research to characterize tertiary oil recovery discharge streams and a review of the new types of chemicals proposed for use in recovery processes in the future.

To design the EPA research program for tertiary oil recovery, it would be useful to convene a seminar of chemical and petroleum industry firms, state regulatory commissions, academic scientists in the relevant disciplines and other Federal agencies. The objectives of the seminar would be numerous. Environmental research priorities could be reviewed and discussed perhaps using an EPA-proposed program as working document. The seminar would provide important channels of information and scientific interchange. EPA could establish informal, voluntary data sources within the industry in order to be apprised of the latest advances in tertary oil recovery processes on a continuing basis. The meeting would also enable EPA to explain its policy objectives and the role of environmental research regarding enhanced oil recovery to the petroleum industry and the scientific community. Research areas to be considered in the design of a comprehensive program are discussed in the following section.

7.4 Research Needs

This study has sought to identify the potential environmental problems which may result from tertiary recovery. In many areas data are either lacking or incomplete with respect to environmental questions. Many of the answers may be sought by the Environmental Protection Agency through monitoring and analysis of field demonstration projects conducted by the Energy Research and Development Administration. To effectively accomplish this research, environmental studies must be integrated into the ERDA demonstration programs. These research needs are:

1. Characterization of and emissions factors for inorganic pollutants from in-situ combustion as functions of process variables, reservoir parameters and oil characteristics.
2. Characterization of and emissions factors for organic pollutants (particularly photochemical oxidants) from in-situ combustion as functions of process variables, reservoir parameters and oil characteristics.
3. Identification and prioritization of all point-and area-sources of hydrocarbon emissions in thermal oil recovery.
4. Cost-benefit analyses of air quality control strategies for thermal oil recovery projects assessing the levels of control attainable impact on oil prices and oil reserves lost as a result of the incremental costs associated with each strategy.
5. Evaluation of field sulfonation processes for manufacture of petroleum sulfonates to assess environmental consequences and economic impact of processes.
6. Evaluation of environmental impact of processes and chemicals used to treat oilfield production emulsions from tertiary recovery.
7. Case studies and modelling of regional groundwater systems to assess the impact of well failure on water supply quality. The Edwards formation in Texas is recommended as one of the areas for further study.
8. Measurement of chemical concentrations in produced water from each of the processes, especially micellar-polymer flooding and in-situ combustion as functions of process variables, reservoir characteristics and oil composition.

9. Assessment of the environmental impact of a change in refinery loads to process and desulfurize a greater proportion of low gravity crude oils resulting from production by thermal methods.

10. Quantification of the physical and chemical factors which may act upon leaks or spills of tertiary oil recovery chemicals. Define limits to degradation processes which may act upon chemicals used in tertiary recovery.

11. Evaluation of the synergistic toxicity (plant and animal) and carcinogenicity of petroleum sulfonates and other materials.

APPENDIX A

GLOSSARY

API Gravity: The standard American Petroleum Institute (API) method for specifying the density of crude oil. It may be calculated from the following formula: Deg API = 141.5/(Sp. gr. 60F)/ - 131.5.

Aquifer: A water-bearing layer of permeable rock, sand, or gravel.

Barrel: A liquid volume measure equal to 42 U.S. gallons.

Biota: Animal and plant life; fauna and flora.

Brine: Water saturated with or containing a high concentration of sodium chloride and other salts.

Btu: British thermal unit; the amount of heat needed to raise the temperature of 1 pound of water 1°F at or near 39.2°F; a measure of energy.

Carcinogen: Substance which may induce cancer.

Cation: The positively charged particle in the solution of an electrolyte which, under the influence of an electrical potential, moves toward the cathode (negative electrode).

Centipoise: A unit of viscosity equal to 0.01 poise. A poise equals 1 dyne-second per square centimeter. The viscosity of water at 20°C is 1.005 centipoise.

Connate Water: Water that was laid down and entrapped with sedimentary deposits, as distinguished from migratory waters that have flowed into deposits after they were laid down.

Core: A sample of material taken from a well by means of a hollow drilling bit. Cores are analyzed to determine their water and oil content, porosity, permeability, etc.

Created Fractures: Fractures induced by means of hydraulic or mechanical pressure exerted on the formation.

Darcy: A unit of permeability. A porous medium has a permeability of 1 darcy when a pressure of 1 atm on a sample 1 cm long and 1 sq cm in cross section will force a liquid of 1-cp viscosity through the sample at the rate of 1 cu cm/sec.

Emulsion: A suspension of one finely divided liquid phase in another.

Fireflooding: *In-situ* combustion.

Forward Combustion: A thermal oil recovery process in which air is injected, and ignition is obtained at the wellbore in an injection well. Continued injectin of air drives the combustion front toward producing wells.

Fracture: Any kind of discontinuity in a body of rock if produced by mechanical failure, whether by shear stress or tensile stress. Fractures include faults, shears, joints, and planes of fracture cleavage.

Gas-Oil Ratio: The number of cubic feet of gas produced with each barrel of oil.

In-situ Combustion: A process which heats oil in the reservoir to increase its mobility by decreasing its viscosity. Heat is applied by igniting the oil sand or tar sand and keeping the combustion zone active by the injection of air.

Interfacial Tension: The contractile force of an interface between two phases.

Miscible: Able to mix together; refers to two or more substances. Liquids that are not miscible separate into layers according to their specific gravities; a substance miscible with each of two immiscible liquids which is used to reduce the interfacial tension between the two immiscible liquids; in oil recovery, a substance miscible with both oil and water.

Miscible Agent: Water is immiscible with oil, and interfacial forces between phases lead to incomplete displacement. Sometimes natural gas can be used as a miscible agent; sometimes miscible agents are injected as slugs, e.g., hydrocarbon gas enriched with LPG.

Miscible Displacement: Displacement of oil by a fluid with which it is miscible. When such a fluid contacts the oil, the two liquids dissolve each into the other and form a single phase. There is no interface between the fluids and hence there are no capillary forces active.

Miscible Displacement Theory: The use of various solvents to increase the flow of crude oil through reservoir rock.

Offset Well: A well drilled near the boundary of a lease opposite a completed well on an adjacent lease.

Oil Saturation: The extent to which the voids in rock contain oil, usually expressed in percent related to total void.

Oil Wet: See Wettability.

pH: A number that represents the negative logarithm, base 10, of the hydrogen-ion activity of a solution. pH < 7 for acid. pH > 7 for alkaline.

Permeability: Capacity for transmitting a fluid. Degree of permeability depends upon the size and shape of the pores and the size, shape and extent of the interconnections. The unit of permeability is the darcy.

Polymer: A very large molecule formed by the combination of many small molecules identical with each other.

Polysaccharide: A carbohydrate containing more than two aldehyde or keto groups.

Pore Volume: The volume of void space in an oil reservoir which may contain petroleum, gas and/or brine.

Porosity: The volume of pore space expressed as a percentage of the total volume of the rock mass; measures the absorbent capacity of the material or the volume of liquid held by the pores.

Reserves: The amount of a mineral expected to be recovered by present day methods and under present economic conditions.

Reservoir: A discrete section of porous rock containing an accumulation of oil or gas, either separately or as a mixture.

Reservoir Fluids: Fluids contained within the reservoir under conditions of reservoir pressure and temperatures; because of this fact their characteristics are different from the characteristics of the same fluids existing under normal atmospheric conditions.

Residual Oil: The amount of liquid petroleum remaining in the formation at the end of a specified production process.

Secondary Recovery: Any method of augmenting the natural energy of a petroleum reservoir to increase production in the second stage of recovery.

Steamflooding: Steam displacement (or steam drive) follows the same basic principle as the waterflood. Steam under pressure is fed into special injection wells, both to heat the oil in place and to drive it to producing wells.

Sulfonates: A surfactant consisting of an organic chain with an SO_3H attached; used in oil recovery because the polar SO_3H end is attracted to water, while the organic end mixes with oil.

Surface Tension: The tension forces existing in the extreme surface film of an exposed liquid surface due to unbalanced cohesive forces within the body of the liquid.

Surfactant: A material which affects the interfacial tension between two liquids. In oil recovery, surfactants are used which reduce the interfacial tension between oil and water. Each surfactant molecule has a polar end, which is attracted to water, and an organic chain, which is attracted to oil.

Sweep Efficiency: The ratio of the volume of rock contacted by the displacing fluid to the total volume of rock subject to invasion by the displacing fluid.

Thermal Recovery: A petroleum-recovery process that utilizes heat to thin viscous oil in an underground formation and allows it to flow more readily towards producing wells.

Viscosity: The internal resistance offered by a fluid to flow. Attributable to the attractions between molecules of a liquid, this phenomenon is a measure of the combined effects of adhesion and cohesion to the effects of suspended particles and to the liquid environment.

Waterflooding: A secondary-recovery operation in which water is injected into a petroleum reservoir to create a water drive to increase production.

Wettability: (As applied to petroleum reservoirs) the relative affinity of the coexisting oil and water phases to adhere to the surface of a rock. If the rock is predominantly in contact with water, it is said to be preferentially water-wet. Similarly, if the rock is predominantly covered with oil, it is referred to as oil-wet.

Wetting: The adhesion of a liquid to the surface of a solid.

Wetting Agent: A substance or composition which, when added to a liquid, increases the spreading of the liquid on a surface or the penetration of the liquid into a material.

APPENDIX B

METHODOLOGY AND RATIONALE

B.1 Estimation of Water Usage (Table 2-4)

The following data on Table B-1 were the assumptions used as a basis for the calculations. Derived data are presented at the bottom of the table.

B.2 Chapter Two -- Fate of Sulfur Compounds and Nitrogen Compounds Created During In-Situ Combustion

The theoretical basis for assuming that all of the sulfur compounds will appear dissolved in the reservoir water and produce water is as follows:

Most sulfur will be present as elemental (Sx), pyritic (FeS) or high molecular weight organics in the residual or coking fractions of the crude oil. Small amounts of sulfur (e.g., thiophene, C_5H_5S) will distill ahead of the firefront, but will probably condense and be produced in the liquid stream (Boiling Point 84.1°C.). In the combustion process, elemental and pyritic sulfur will burn to form sulfur dioxide and organics will pyrolyze. Since not all the oxygen is consumed in the formation, oxygen is available ahead of the burning region for further oxidation of sulfur and sulfur dioxide. Water solubility of sulfur dioxide is low at high temperatures and low pH. However, oxidation of sulfur dioxide in aerated water is rapid in the presence of ferric ions (Fe^{+3}).

Air oxidation of sulfur dioxide is very complex. The reaction is thermodynamically favored, but is very slow in the absence of a catalyst. Within the oil reservoir, several catalysts may be present. Coke will be like activated carbon and siliceous sandstones may offer active sites. Ferric ion or vanadium may act as catalysts in aerated water. In addition, the distance between injection and producing wells of 400 feet or more provides sufficient mixing length to produce sulfuric acid. This conclusion is supported by the low pH values for produced waters in firefloods which may be attributed to the production of sulfuric acid in the formation.

TABLE B-1

ASSUMED OIL AND MICELLAR FLOOD CHARACTERISTICS FOR ESTIMATION OF WATER USAGE

TYPE MICROEMULSION	OIL EXTERNAL		WATER EXTERNAL	
WATER QUALITY	HIGH	LOW	HIGH	LOW
Oil Saturation (initial)	30%	30%	30%	30%
Recovery %	50%	40%	50%	40%
Water in Micellar Solution[a]	50%	50%	90%	90%
Preflush (PV)	0.05-0.1	0.01-0.2	0.03-0.5	0.5-1.0
Micellar Solution (PV)	0.03-0.08	0.03-0.08	0.10-0.25	0.10-0.25
Mobility Buffer (PV)	0.4-0.6	0.4-0.6	0.4-0.6	0.4-0.6
Drive Water (PV)	0.5-0.6	0.5-0.6	0.5-0.6	0.5-0.6
Calculations:				
Oil Recovery (BBL) per (PV)	0.15	0.12	0.15	0.12
Water Usage (per BBL oil covered)				
Preflush:	0.33-0.67	0.8 - 1.7	2.0 - 3.3	3.3 - 6.7
Slug:	0.1 - 0.27	0.12 - 0.3	0.6 - 1.5	0.75- 2.0
Buffer:	2.7 - 4.0	3.3 - 5.0	2.6 - 4.0	3.3 - 5.0
Drive:	3.3 - 4.0	4.2 - 5.0	3.3 - 4.0	4.2 - 5.0
Total	6.5 - 9	8.5 - 12	9.5 - 13	11.5 - 19

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[a] Other stages of flood are assumed to be approximately all water.

Similarly, oxides of nitrogen, which are probably produced in much smaller quantities at typical in-situ combustion temperatures of 700-1,200°F, may be converted to nitric acid in the formation. These are some situations in fireflooding which require further study. The composition of the emissions may change as the firefront approaches the producing well due to a decreased mixing length and other factors. Operation of a fireflood at non-optimum conditions may also alter the produced gas stream. In particular, since air injection is expensive, operation of a "lean" fireflood could produce more sulfur dioxide. Conversely, operation of a "rich" flood might result in larger output of nitrogen compounds.

B.3 Identification of Technically Feasible Projects

Project sites for the various tertiary oil recovery processes were identified by Energy Resources and Core Laboratories through an appraisal of the suitability of reservoir and oil characteristics in more than 800 discrete reservoirs in 381 major oil fields in the on-shore contiguous United States. In some instances, especially in Texas, Oklahoma and Kansas, insufficient data were available to assess definitively the technical feasibility of tertiary oil recovery in the reservoir. However, the review of discrete reservoirs often revealed possibility for several methods of tertiary oil recovery within the same field. For each field, data were considered on water composition (if available), average porosity, average permeability, depth, lithology, drive mechanism, temperature gradient, oil viscosity, permeability variation, presence of fractures, and past production history. Few rigid limitations were placed on the assessment. Surfactants and polymers were assumed stable up to 200°F and micellar-polymer flooding was considered effective on oils with a viscosity less than 10 centipoise. Steam processes were considered feasible at depths up to 3,000 feet; in-situ combustion, 5,200 feet. Carbon dioxide injection was considered infeasible in oil reservoirs shallower than 6,500 feet. Generally, sandstone reservoirs were the type considered as feasible with the exception of oolitic limestone formations. Other factors were weighed on a case-by-case basis.

Throughout the assessment, the economics of individual fields were set aside. Factors are recognized such as development/drilling pattern in existence, size of reservoir, oil saturation, reservoir thickness, availability of raw materials that will influence the size and economic feasibility of any tertiary recovery project undertaken in the field. The location and timing of actual tertiary oil recovery projects will depend upon the interaction of political, technical, economic and environmental factors.

Revision, updating or estimating of the production potential from tertiary oil recovery through consideration of the possible interactions of these factors was beyond the scope of this study as defined. In order to estimate regional potentials for tertiary oil recovery, available estimates of the national production potential were allocated among the technically feasible projects. The technical assessment occasionally revealed that more than one recovery technique might be feasible in a given reservoir within a field. In such cases, both types of projects were counted. For each recovery process, the number of projects within the region was tabulated. The massive nature of the shallow reservoirs in California which are amenable to thermal methods required favorable weighting of these projects by a factor of 10 in order to reach reasonable agreement with Bureau of Mines estimates of potential oil recovery there. The national estimates were then allocated proportionally to the regions based on the number of reasible projects identified. Given the other sources of variation in the amount of oil eventually produced by tertiary methods the approach is useful. One problem which does occur is an understatement of the potential for the Rocky Mountain region. This problem arises because of the lack of suitable "giant" oil fields in the region, insufficient reservoir data and a large number of small or "near giant" fields in the area which might be feasible for tertiary recovery but were not evaluated.